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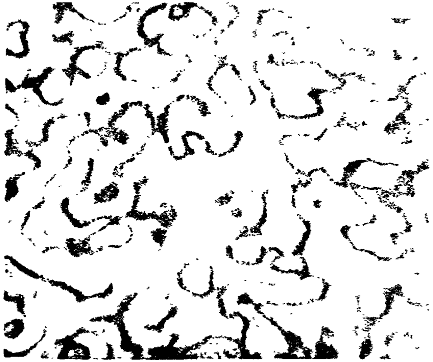
Frontispiece.

A Grey Iron containing 2 per cent silicon and 1 per cent phosphorus, heat tinted, showing graphite (black), solid solution of silicon in iron (yellow) and phosphide of iron (blue).



B Slowly cooled phosphor bronze heat tinted, showing copper (red) non-homogeneous solution of tin in copper (shading from white to blue-grey) and phosphide of copper (yellow).

ALLOYS

AND THEIR INDUSTRIAL APPLICATIONS.

BY

EDWARD F. LAW,
ASSOCIATE OF THE ROYAL SCHOOL OF MINES

With Numerous Illustrations and Plates.

FOURTH EDITION.

LONDON:
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EXETER STREET, STRAND, W.C. 2.
1919.

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PREFACE TO THE SECOND EDITION.

In the preparation of the new edition of this book an attempt has been made to bring the information up to date by including the results of recent research and invention, while at the same time retaining the features of the first edition.

Since the publication of the first edition an immense amount of purely scientific research work has been carried out which is beyond the scope of the present volume. Fortunately, however, there is the less reason to include an account of this work inasmuch as the purely scientific aspect of the subject has been ably dealt with in Gulliver's *Metallic Alloys* and Desch's *Metallography*.

The necessity for a new edition appears to justify the author's belief that there is some demand for a book which deals with the practical side of scientific research, and which endeavours to translate the results of such research and render them intelligible to the practical man

The author is again indebted to many friends for valuable assistance. For many of the illustrations he has to thank Messrs Zeiss, Reichert, The Morgan Crucible Co., The London Emery Works, Alldays & Onions, and the President and Council of the Iron and Steel Institute. Lastly, he wishes to thank those friendly critics who have made suggestions for the improvement of the book. Such suggestions have been adopted wherever it was possible to do so without altering the character and scope of the volume.

E. F. L.

Manchester, *March* 1914.

PUBLISHERS' NOTE TO THIRD EDITION.

The war has demonstrated the immense value of scientific research translated into practice, and this book, with others of our "Recent Research Handbooks," has proved of great service, so that the edition has been exhausted suddenly, and the author is too much occupied to make revision, and this reprint is issued

May 1917.

[*Reprinted for Fourth Edition*.]

PREFACE TO THE FIRST EDITION.

It is now nearly seven years since the late Sir William C. Roberts-Austen asked the author of this treatise (who was at that time his assistant) to help him in the preparation of a book on Alloys. Unfortunately that work was never completed, for before it had advanced beyond the preliminary stages, the illness from which Sir William had been suffering terminated fatally, and the science of metallurgy lost its most brilliant exponent. And so it is that, to the regret of all his admirers, there is no comprehensive treatise on the subject of alloys by the man who made it a lifelong study, and who did more than any other to raise it to the important position which it occupies at the present time. It was at first hoped that the work might be completed, but the available material was insufficient and too disconnected to be suitable for the purposes of a text-book, and the project had to be abandoned. Subsequently, at the request of the publishers, the author undertook to write a book on Alloys to fill the gap in their Metallurgical Series.

During the last few years an enormous amount of research work has been carried out with the object of determining the nature and physical properties of alloys, and much valuable information has been accumulated. This information, which deals mainly with the simple alloys of two metals, is scattered throughout the numerous periodicals and publications in which the original communications have appeared, and up to the present no attempt has been made to collect the facts or to apply them to the more complex commercial alloys.

Moreover, much of the work is of a purely scientific nature, and written in a style which is hardly calculated to appeal to those who are not in close touch with recent advances in physical science. The manufacturer, for example, may be readily excused for hesitating to plunge into the intricacies of solid solutions, hyper-eutectics, solidus curves, and phases. In this volume, therefore, an attempt has been made, first, to summarise the existing state of our knowledge of mixed metals, paying special attention to the general principles and essential facts while omitting all unimportant details, and secondly, to apply that knowledge to the industrial alloys in everyday use. An attempt has also been made to present the subject in such a manner that it will be intelligible not only to the student but also to the manufacturer and the engineer, for whom, indeed, the volume is primarily intended.

The complete freezing-point curves and the photo-micrographs have been made a special feature of the book, and it is hoped that they will prove useful. The freezing-point curves have been entirely replotted to one uniform scale, so that they are strictly comparable, while the photographs, with one or two exceptions, are taken from samples of commercial alloys and not from small samples made in the laboratory. It will also be noticed that the magnifications employed are in most cases 100 and 1000 diameters respectively. Experience has shown that these magnifications fulfil all that is necessary in the great majority of cases, but the important point is that the magnification should always be the same, so that the mind may easily and instinctively compare the size of grain, constituents, flaws, etc. The importance of this is not sufficiently appreciated, and it would be well if authors would adhere, as far as possible, to certain standard magnifications.

The colour photographs reproduced in the frontispiece, illustrating the heat tinting of alloys, were taken by the author on Lumière autochrome plates, and were the first examples of the practical application of colour photography to metallography.

The author desires to express his gratitude to many friends for kind assistance, more especially to Mr R. Lagerwall of the Phosphor Bronze Company, and Mr Parsons of the Manganese Bronze and Brass Company, who have kindly supplied him with samples and information; Mr A. J. Williams, who has supplied samples of magnalium alloys, and Messrs Carl Zeiss and W. Watson, who have supplied the illustrations of photo-micrographic apparatus. To Mr J. H. Blakesley the author is indebted for many useful suggestions and kind help in reading and correcting the proofs.

Lastly, the author thankfully acknowledges his great indebtedness to his friend the late Mr Bennett H. Brough, whose technical and literary skill and large experience were ever available in all matters in which counsel was sought. In the press of his own exceptionally busy life he always found time to help, and ungrudgingly gave of his wide knowledge. This generous assistance and unfailing kindness will ever remain the pleasantest memory connected with the preparation of this volume.

EDWARD F. LAW.

January 1909.

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PHYSICAL CONSTANTS OF METALS.

Metal	Symbol	Atomic Weight	Atomic Volume	Specific Gravity	Specific Heat	Melting Point °C	Coefficient of Linear Expansion	Thermal Conductivity in cal cm secs	Electrical Conductivity Ag = 100
Aluminium	Al	27·1	10·6	2·56	0·218	657	0·0000231	0·502	57·3
Antimony	Sb	120·2	17·9	6·71	0·051	630	0·0000105	0·042	4·6
Arsenic	As	75·0	13·2	5·67	0·081	450	0·0000055		4·7
Barium	Ba	137·4	36·5	3·78	0·047	850			1·3
Bismuth	Bi	208·0	21·2	9·80	0·031	268	0·0000162	0·019	1·3
Cadmium	Cd	112·4	13·0	8·60	0·056	321	0·0000306	0·219	14·7
Cæsium	Cs	132·8	71·1	1·87	0·048	26			3·7
Calcium	Ca	40·1	25·5	1·57	0·170	780			22·1
Cerium	Ce	140·2	21·0	6·68	0·045	623			
Chromium	Cr	52·0	7·7	6·80	0·120	1482			
Cobalt	Co	59·0	6·9	8·50	0·103	1464	0·0000123		15·6
Columbium	Cb	93·5	7·4	12·70	0·071				
Copper	Cu	63·6	7·1	8·93	0·093	1084	0·0000167	0·924	94·0
Gallium	Ga	69·9	11·8	5·90	0·079	30			
Glucinum	Gl	9·1	4·7	1·93	0·621				
Gold	Au	197·2	10·2	19·32	0·031	1063	0·0000144	0·700	66·8
Indium	In	114·8	15·5	7·42	0·057	155	0·0000417		16·5
Iridium	Ir	193·1	8·6	22·42	0·033	1950	0·0000070		
Iron	Fe	55·8	7·1	7·86	0·110	1505	0·0000121	0·147	16·2
Lanthanum	La	139·0	22·4	6·20	0·045	810			
Lead	Pb	207·1	18·2	11·37	0·031	327	0·0000292	0·084	7·2
Lithium	Li	6·9	13·0	0·54	0·941	186			17·5
Magnesium	Mg	24·3	14·0	1·74	0·250	633	0·0000269	0·343	33·7
Manganese	Mn	54·9	6·9	8·00	0·120	1207			
Mercury	Hg	200·6	14·7	13·59	0·032	−39	0·0000610	0·020	1·6
Molybdenum	Mo	96·0	11·2	8·60	0·072	2500			
Nickel	Ni	58·7	6·7	8·90	0·108	1427	0·0000127	0·141	21·2
Osmium	Os	190·9	8·5	22·48	0·031	2500	0·0000065		15·5
Palladium	Pd	106·7	9·3	11·50	0·059	1545	0·0000117	0·168	14·5
Platinum	Pt	195·2	9·1	21·50	0·032	1710	0·0000089	0·166	13·4
Potassium	K	39·1	45·5	0·86	0·170	62	0·0000841		20·8
Rhodium	Rh	102·9	8·5	12·10	0·058	1660	0·0000085		
Rubidium	Rb	85·5	55·9	1·53	0·077	38			..
Ruthenium	Ru	101·7	8·3	12·26	0·061	1800	0·0000096		
Silver	Ag	107·9	10·2	10·53	0·056	961	0·0000192	0·993	100·0
Sodium	Na	23·0	23·8	0·97	0·290	95	0·0000710	0·365	37·3
Strontium	Sr	87·6	34·5	2·54		800			6·7
Tantalum	Ta	181·5	16·9	16·80	0·036	2910	0·0000079		8·9
Tellurium	Te	127·5	20·4	6·25	0·049	440	0·0000167		6·8
Thallium	Tl	204·0	17·2	11·85	0·033	303	0·0000302		8·3
Thorium	Th	232·4	20·9	11·10	0·028				
Tin	Sn	119·0	16·3	7·29	0·055	232	0·0000223	0·155	11·3
Titanium	Ti	48·1	9·9	4·87	0·130				
Tungsten	W	184·0	9·6	19·10	0·034	3100			1·7
Uranium	U	238·5	12·8	18·7	0·028				
Vanadium	V	51·0	9·3	5·5	0·125	1680			..
Yttrium	Yt	89·0	[illegible]	3·80					
Zinc	Zn	65·4	9·1	7·15	0·094	419	0·0000291	0·269	25·2
Zirconium	Zr	90·6	21·8	4·15	0·066	1500			

ALLOYS.

CHAPTER I.

INTRODUCTION.

There has been some difference of opinion as to the origin of the word alloy, but according to Roberts-Austen it is derived from the Latin word *alligo* (*ad ligo*), "to bind to," and refers to the union or binding together of the metals constituting the alloy.

From the earliest times alloys were produced accidentally by the simultaneous reduction of mixtures of metallic ores, but there is little doubt that the first metals to be intentionally alloyed were the precious metals, and more especially gold, and it is equally certain that these attempts to alloy the precious metal were of a fraudulent character, and carried out with the object of producing a metal which might be substituted for the pure metal. How long those fraudulent but successful practices were carried on without any adequate means of detection it is impossible to say, but they received their first check when Archimedes conceived the brilliant idea that all bodies when immersed in water must displace their own volume of water irrespective of their weights, and that their weights in water would be less than their weights in air by the weight of the water thus displaced. From this he argued that if gold were alloyed with another metal its presence could be detected by determining the displacement in water, and the story of his detection of the addition of an alloy to the gold used in making the king's crown is too well known to need repetition.

The alloying of gold and silver plays a prominent part throughout the entire history of the metals, and this probably accounts for the fact that the word alloy, as ordinarily used in the English language, signifies a depreciation or lowering of value. Thus we frequently read of "unalloyed pleasure" and "unalloyed happiness," and the definition of the word in some dictionaries is "to add base metal." To the metallurgist, however, the word conveys a very different meaning, and the object he aims at in alloying metals is to produce a new metal whose properties shall be superior to those of the metals of which it is composed.

Probably the most satisfactory definition of an alloy is that which describes it as "a mixture of two or more metallic substances which, after melting, does not separate into two distinct layers." But commercial enterprise refuses to be bound by definitions, and so we find commercial alloys which on cooling *do* separate into layers, if special precautions are not taken to prevent them doing so, and as the object of this volume is to deal with the commercial alloys we must perforce find a definition which will include them. For this purpose, then, we will define an alloy as "a coherent metallic mass produced by the intimate mixture, whether by fusion or otherwise, of two or more metals or metallic substances." By the addition of the words "metallic substances" the definition may be made to include those alloys of the type of phosphor-copper which are really alloys of a metal with a definite compound (such as phosphide of copper) whose appearance and properties may be regarded as metallic.

The importance of the study of metallic alloys is evident when we consider the extent to which they are employed and the comparatively limited uses of metals in the pure state. Iron, for example, in the pure state has a tensile strength of only 16 tons per sq. in., and even the use of wrought iron, which is the purest commercial form of iron, is comparatively insignificant compared with the use of steel, which must be regarded as an iron alloy. It is true that copper in a pure state is employed for a number of purposes, but the amount of pure copper used is only a fraction of the copper used in the form of bronze, brass, German silver, and a number of other copper alloys. Gold and silver are practically never employed in an unalloyed condition. Lead, zinc, tin, nickel, and aluminium are all used to a certain extent in the pure state, but their alloys account for a very large proportion of the annual consumption of these metals.

Preparation of Alloys.—In addition to the obvious method of melting together the component metals, alloys may be prepared in several other ways. Some of these are of purely theoretical interest, while others have been, and are still, used commercially. The methods of preparation may be regarded as six in number:—

(1) By sublimation or condensation of metallic vapours.
(2) By compression.
(3) By diffusion.
(4) By electro-deposition
(5) By the simultaneous reduction of two or more metals.
(6) By simple melting of the constituent metals.

(1) **Sublimation or Condensation of Vapour.**—The formation of alloys by condensation of metallic vapour is rare, but such cases have been observed to occur in furnace products, and it is probable that certain alloys which are found in the native state have been formed in this way By the decomposition of mixtures of the carbonyls of iron and nickel, alloys of these metals may be produced.

Alloys may also be formed by the action of the vapour of one metal upon another. Thus copper exposed to the action of zinc vapour is rapidly converted into brass. An example of the practical application of this property to commercial purposes is to be found in the so called "dry galvanising" process known as Sherardising. In this process the zinc vapour alloys with the iron or steel and forms a perfectly adherent coating.

(2) **Compression.**—In 1878 Spring showed that if metals in a finely divided state are subjected to pressure the particles unite to form a solid mass, as though they had been melted, although the actual rise in temperature, due to the increase of pressure, is inconsiderable. The pressure required to cause particles of metals to unite in this way depends upon the nature of the metal, but the following figures have been determined for several of the common metals:—

Lead	unites at	13	tons	per sq. in.
Tin	,,	19	,,	,,
Zinc	,,	38	,,	,,
Antimony	,,	38	,,	,,
Aluminium	,,	38	,,	,,
Bismuth	,,	38	,,	,,
Copper	,,	33	,,	,,

With increasing pressure the metals can be forced through a hole in the base of the compression chamber in the form of wire. In the case of lead and tin the pressures required to effect this are 33 and 47 tons per sq. in. respectively.

If now, instead of compressing simple metallic powders, mixtures of different metals are subjected to the same treatment it should be possible to produce alloys, and Spring showed that this is actually the case and that true alloys are so formed. Thus a mixture of bismuth, lead, tin, and cadmium in the proportions of 15, 8, 4, and 3 parts respectively gave a fusible alloy which melted at 98°, a temperature no less than 134° lower than the melting-point of the most fusible of the constituents, tin, which melts at 232°.

(3) **Diffusion.**—The diffusion of metals will be considered later in some detail, and it is only necessary to point out here that alloys can be formed by the diffusion of solid metals in contact with one another even at ordinary temperatures, as shown by Roberts-Austen in the case of lead and gold.

(4) **Electro deposition.**—If an electric current is passed through a solution containing two metallic salts it is possible, under suitable conditions, to obtain the two metals deposited at the same time in the form of a true alloy. It is only possible to obtain the proper conditions with a few combinations of metals, but the method is used commercially to deposit brass from solutions containing copper and zinc, and was at one time employed for electroplating with alloys of silver and cadmium in place of pure silver. From a commercial point of view the process presents many difficulties, and is only practicable in the case of a limited number of alloys.

(5) **Simultaneous Reduction of Metals.**—This is the primitive method by which alloys were made long before the metals of which they were composed were known in the free state. Thus brass was well known and largely used long before the metal zinc was known, and in later times the regular method of making brass, known as the "calamine method," consisted in reducing calamine in the presence of metallic copper. A still more recent application of the method is to be found in the production of aluminium bronze by the Cowles' process, in which the reduction of aluminium was carried out in an electric furnace in presence

of metallic copper which immediately alloyed with the reduced aluminium.

Although many of these processes are now obsolete, a number of alloys are still manufactured by the simultaneous reduction of two metals. Ferro-manganese and spiegeleisen are manufactured in the blast furnace by the simultaneous reduction of iron and manganese ores, while ferro-chrome, ferro-silicon, and ferro-phosphorus are made both in the blast furnace and in the electric furnace; and ferro-titanium, ferro aluminium, and more complex alloys (such as ferro-aluminium silicide and ferro calcium silicide) are made in the electric furnace

An interesting example of the return to ancient methods in the production of alloys is to be found in the case of Monel metal, an alloy consisting essentially of nickel and copper, which is largely used in America and is obtained by smelting together the mixed nickel and copper ores as they occur in the mines at Copper Cliff, Ontario. By this means it has been found possible to produce an alloy possessing valuable physical properties direct from the ore without incurring the expense of first separating and refining the metals and then alloying them in suitable proportions.

Another method of producing alloys by simultaneous reduction to which some reference must be made is that commonly known as the Goldschmidt or thermit process, which depends on the powerful affinity of aluminium for oxygen, whereby it is able to combine with the oxygen of many other metallic oxides, leaving the metals in a free state. The reaction may be represented thus:—

$$3CuO + 2Al = 3Cu + Al_2O_3.$$

The heat produced by the reaction is so great that if the oxide is merely mixed with granulated aluminium and heated in a furnace the reduction often takes place with explosive violence and a method must be adopted of controlling the reaction. The usual procedure is as follows:—A small quantity of the oxide or oxides to be reduced is mixed with the calculated quantity of granulated aluminium and placed in a crucible which has been previously lined with magnesia in order to resist the high temperature. On the top of the mixture is placed a small heap of an ignition powder made by mixing powdered aluminium with an easily reducible oxide, such as barium or sodium peroxide, and into this heap is inserted a short piece of magnesium wire or cordite. The ignition of the magnesium wire is sufficient to start the reaction in the ignition powder, which is then communicated to the mixture in the crucible. When the reaction is fairly started the remainder of the oxide to be reduced, mixed with the requisite amount of aluminium, is slowly charged into the crucible. If this is carried out properly the reduced metal will settle to the bottom of the crucible under a layer of slag consisting of fused alumina. This method is of much service in preparing alloys, as many of the oxides of the rare metals are readily reduced by aluminium; but it is often difficult to obtain the metals free from a certain amount of aluminium. On the other hand, the metals and alloys obtained by this process are entirely free from carbon, which for many purposes is a very important consideration. The heats of formation given in the following table will indicate the relative reducibility of the oxides, and a simple calculation will give the heat evolved during the reaction. Thus in the case of the reduction of nickel oxide

$$3NiO + 2Al = 3Ni + Al_2O_3$$

we have the heat of formation of Al_2O_3 ($131·2 \times 3 = 393·6$) less the heat of formation of 3NiO required for the reduction ($61·5 \times 3 = 184·5$), leaving 209·1 calories. This excess heat has been employed in the welding of tram rails and emergency repairs of all sorts of fractures, as the operation can be carried out wherever required and quite independently of the existence of furnaces.

HEAT OF FORMATION OF OXIDES.

METALS.

Magnesium (MgO)	145·5	calories.
Calcium (CaO)	145·0	,,
Strontium (SrO)	131·0	,,
Aluminium $\left(\frac{Al_2O_3}{3}\right)$	131·2	,,
Barium (BaO)	124·2	,,
Sodium (Na_2O)	100·9	,,
Potassium (K_2O)	98·2	,,

Silicon $\left(\frac{SiO_2}{2}\right)$	90·9 calories.
Boron $\left(\frac{Bo_2O_3}{3}\right)$	90·9 ,,
Manganese (MnO) .	90·0 ,,
Zinc (ZnO)	84·8 ,,
Tin $\left(\frac{SnO_2}{2}\right)$	70·6 ,,
Cadmium (CdO)	66·3 ,,
Iron $\left(\frac{Fe_2O_3}{3}\right)$.	65·9 ,,
Tungsten $\left(\frac{WO_2}{2}\right)$	65·7 ,,
Cobalt (CoO) .	64·5 ,,
Nickel (NiO) .	61·5 ,,
Antimony $\left(\frac{Sb_2O_3}{3}\right)$	55·6 ,,
Arsenic $\left(\frac{As_2O_3}{3}\right)$	52·1 ,,
Lead (PbO)	50·8 ,,
Bismuth $\left(\frac{Bi_2O_3}{3}\right)$	46·4 ,,
Copper (Cu_2O)	43·8 ,,
Mercury (HgO)	21·5 ,,
Silver (Ag_2O) .	7·0 ,,
NON METALS.	
Carbon (CO) .	68·2 ,,
Hydrogen (H_2O) .	58·1 ,,
Phosphorus $\left(\frac{P_2O_5}{5}\right)$.	73·1 ,,
Silicon $\left(\frac{SiO_2}{2}\right)$.	90·9 ,,
Sulphur $\left(\frac{SO_2}{2}\right)$.	34·6 ,,

(6) **Melting the Constituent Metals.**—All the well-known alloys, such as bronze, brass, German silver, pewter, and other white metal alloys, gold and silver alloys, etc., are made by melting together the metals which are to be alloyed. The melting is nearly always performed in crucibles; but in a few cases, where large ingots or castings are required, reverberatory furnaces are employed.

Reverberatory Furnaces.—These furnaces, which are capable of melting several tons of metal, are coal fired, the consumption of coal when gun-metal is being melted amounting to about 20 per cent. of the weight of the charge. The metal is tapped into ladles, which are taken by overhead cranes to the casting floor. The following charge sheet of a 7-ton furnace, melting No. 1 Admiralty gun-metal, is given by Primrose, and will serve as an example of reverberatory melting practice:—

CHARGE SHEET OF 7-TON REVERBERATORY FURNACE.

Charge.		Copper.		Tin.		Zinc.		Lead.	
Material	Weight cwts.	Per cent.	Cwts per cent.	Per cent.	Cwts. per cent.	Per cent	Cwts. per cent.	Per cent.	Cwts. per cent
Shop scrap . .	20	87·8	1,756	9·5	190	2·0	40	0·7	14
Bought-in scrap .	59	85·5	5,044	8·5	501	5·0	295	1·0	59
Machine borings	20	87·7	1,754	9·5	190	2·0	40	0·8	16
Copper ingots	36	100·0	3,600	...			...		..
Tin ingots . .	5	...	.	100·0	500			...	
Total . .	140	...	12,154	.	1381	...	375		89
Average calculated analysis		86·8	..	9·87	...	2·7	...	0·63	.
Actual analysis .		87·9	...	9·5	...	2·0	..	0·60	..

Charged, 10 a.m. to 12 noon; tapped, 4.30 p.m.

Fuel consumption; 30 cwts. (Splint coal).

Crucible Furnaces.—The crucibles used in the manufacture of alloys are either made of fireclay or of a mixture of fireclay and graphite. The former are used for the melting of iron alloys, where carbon plays an important part in the composition of the alloy; while the latter, which are known as graphite or plumbago crucibles, are used for all oxidisable alloys, such as those of copper.

The furnaces in which the crucibles are heated may be either coke, gas, or oil fired, the type most commonly employed in this country being the old-fashioned, natural draft, coke-fired pot furnace. Several of these furnaces are arranged in a row at the floor level, the flues running into a main flue connected with the stack. In front of the furnaces are the ashpits, covered by a grating on which the melters stand. For crucibles containing more than

100 lbs. of metal and which are drawn from the furnace by crane or pulley blocks, the furnace top should be level with the floor; but for crucibles taking less than 100 lbs. and which are withdrawn by hand, the furnace top should be about 10 ins. above the floor level, so that by placing one foot against the furnace the melter can steady himself and use his strength to greater advantage. The consumption of coke in natural draught, coke-fired furnaces is about 20 to 25 lbs per 100 lbs. of brass melted.

Instead of using a number of comparatively small crucibles, it is often desirable to employ one large crucible, and to avoid the difficulty and danger of handling large crucibles full of molten metal the crucible is fixed in the furnace, which is so constructed that it can be tilted and the metal poured into a preheated ladle or direct into the moulds Forced draught is employed, the air, at a pressure of 1½ to 2 ins. of water, being supplied by means of a motor blower or fan. One of the best known of these furnaces is the Morgan tilting furnace shown in fig. 1. This furnace is constructed on the regenerative principle, the incoming air and waste gases passing through pipes arranged concentrically in such a way that the air travels in a spiral direction round the flue and becomes heated before entering the furnace A preheater is fitted to the furnace, and by means of a handle and cam can be easily raised and swung free from the furnace before skimming and pouring. A special feature of this furnace is the tilting device, which is so arranged that the axis upon which the furnace is tilted is immediately below the spout of the crucible, so that the pouring-point is constant. Other types are made with portable bodies which can be removed to any part of the foundry by means of an overhead crane

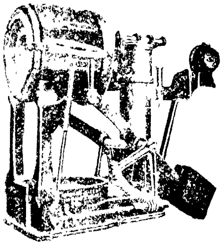


FIG. 1.—Morgan's Coke-fired Tilting Furnace.

The consumption of fuel in these furnaces is very much lower than in the old fixed type, and at the same time the life of the crucibles is very materially lengthened. It is reckoned that the saving in crucibles amounts to about 25 per cent., and the saving in fuel at least 10 to 15 per cent. In a series of trials the average life of a crucible when melting brass was found to be forty-six heats; and when used for ordinary foundry purposes, melting gun-metal, phosphor bronze, etc., the average life of a crucible of 400 lb. size was found to be close on forty heats.

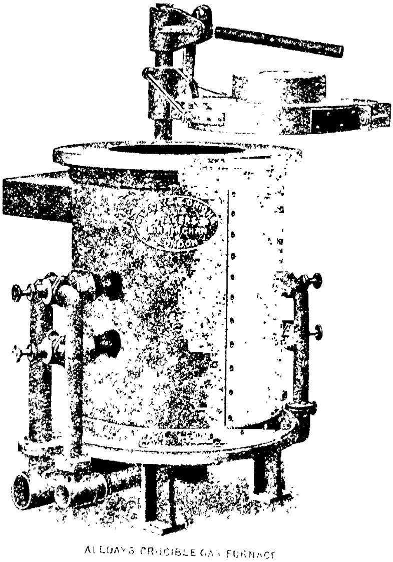


FIG. 2.—Alldays' Gas-fired Crucible Furnace.

The following figures have been given by Hughes as showing a day's work of a crucible tilting furnace in a railway foundry. The fuel used was Durham coke containing 9·35 per cent. of moisture.

Both lift-out and tilting types of furnace may be fired by oil or gas, the selection of the fuel depending upon the conditions of supply and the alloy to be melted. Fig. 2 shows a stationary gas-fired furnace by Messrs Alldays and Onions, and fig. 3 a

Heat.		Time		Ammoter Reading.	Blast Inches H_2O.	Details of Charge							Charge			Yield			Per cent. Loss on each Heat	Coke used.			Remarks
No.	Kind.	Start.	Finish.			Cu.	Pb	Sn.	Zn.	Ingot Metal.	Scrap.	P.Cu	Cwt.	qr.	lb.	Cwt	qr.	lb.		Cwt	qr	lb	
1	Gun-metal	6.30	7.30	1 6	2½	352		40	8				3	2	8	3	2	3¾	1·06	0 0	2 2	2 9	Coke used for starting.
2	Slide valve	8 a.m.	9 15	1·6	2¾	160	10	20		48	200	10	4	0	0	3	3	24	0·90	0	2	9	Scrap = old slide valves.
3	Injector metal	10 0	11 15	1·6	2¾	164	5	20½	10½	250½			4	0	2½	3	3	27	0·77	0	2	9	
4	Brazing ,,	11.30	12.25	1·6	2¼				2	(special) 448½			4	0	2½	3	3	17½	2·88	0	2	9	
5	Copper	1.10	2.15	1 6	3	345			5				3	0	11	3	0	11	0·85	0	2	9	For tube-hole bushes and plugs.
6	Injector metal	2.45	4.15	1·6	3	164	5	20½	10	248			4	0	0	3	3	24	0·90	0	2	9	
	7 hours = 2·8 H.P. hours.												22	2	27	22	1	23¼	7·36	4	0	0	= 19·69 lbs. of coke per cwt of metal melted

tilting furnace by the same firm suitable for gas or oil. Fig. 4 is another type of oil-fired tilting furnace by the Morgan Crucible Co. Another type of oil-fired furnace, which resembles a reverberatory furnace on a small scale rather than a crucible furnace, is the Charlier rolling furnace shown in figs. 5 and 6. It is cylindrical in form, and is mounted on two cast-iron standards having half-bearings, so that the body of the furnace can be picked up by a crane when desired. For this purpose the furnace may be fitted with a forged steel yoke. A blast of 14 to 18 ins. pressure is used, and the consumption of oil for general foundry work is said to be two to three gallons per cwt. of metal.

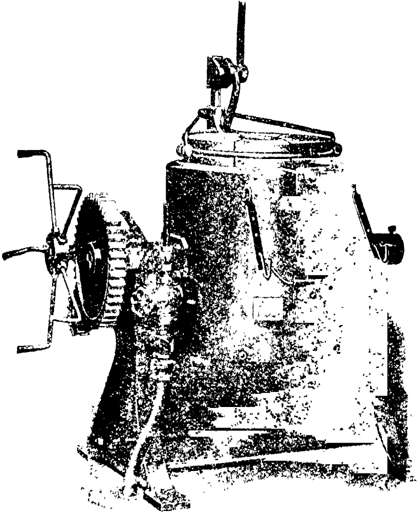


FIG. 3.—Alldays' Tilting Furnace for Oil or Gas.

In America, where oil is readily obtainable, it is very largely used, but in this country the low price of coke has hitherto prevented any serious competition by oil in spite of its many advantages. However, recent improvements in the design of the furnaces have greatly increased their efficiency, and in many

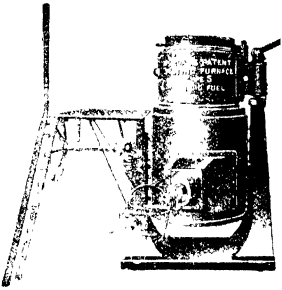


FIG. 4.—Morgan's Oil fired Tilting Furnace.

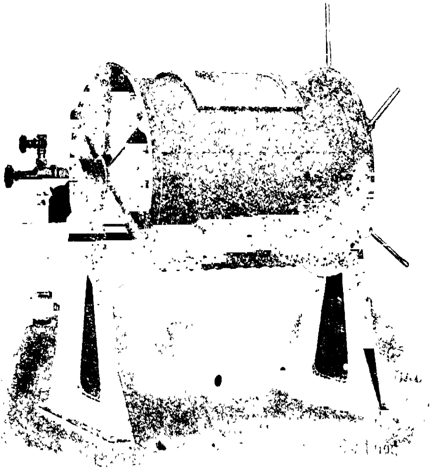


FIG. 5.—Charlier Rolling Furnace.

cases they are taking the place of coke-fired furnaces Fig. 7 shows a twin-chambered stationary furnace in which the waste heat from one chamber is led into a second chamber and utilised for preheating the second charge of metal. Fig. 8 shows the Buess tilting furnace, in which the compressed air is led into the base of the furnace so that it becomes heated and at the same time tends to cool the bottom of the furnace where excessive heating and destruction of the lining most commonly occur. The heated air is then passed through the oil chamber and renders the oil more fluid, thus preventing troubles due to the clogging of the burner. The saving in labour when using oil-fired furnaces is considerable, as the carting of fuel and removal of ashes is dispensed with, and no stoking of the furnace while in operation or removal of clinker, etc., after the day's run is necessary.

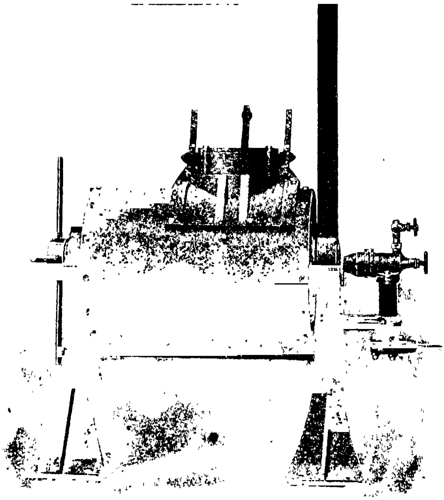


FIG. 6.—Charlier Rolling Furnace for lifting by Crane.

In both oil- and gas-fired furnaces the ease with which the temperature can be regulated is a great advantage, and the recovery of a charge in the event of the breaking of a crucible is a further advantage, especially in the melting of the rarer metals. Much depends, however, on the nature of the metal to be melted. Thus there is a prevalent belief among many melters of aluminium that in oil-fired furnaces it is difficult to prevent serious oxidation of the metal, and pressure gas is now being largely used in aluminium foundries, as it is claimed that by its use oxidation troubles are reduced to a minimum. On the other hand, there is little doubt that in the melting of gold and silver the losses due to volatilisation are greater in gas-fired furnaces than in those using coke. These examples are merely quoted in order to show that many factors come into play in the melting of the different metals, and these factors must be considered in the selection of a fuel suitable for the particular metal or alloy to be melted.

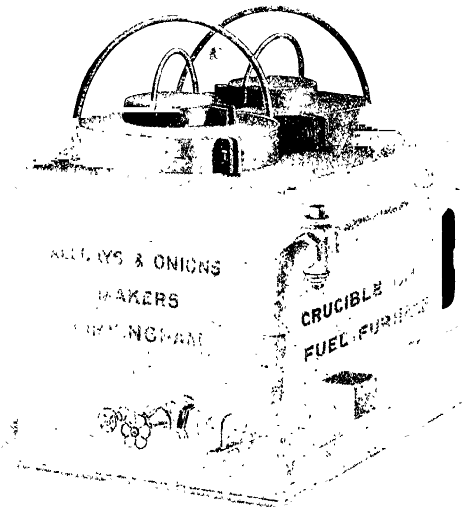


FIG. 7.—Alldays' Twin-chamber Oil-fired Furnace.

Electric Furnaces.—Electric furnaces are now largely used in the manufacture of high grade steel, and so much has been said and written in praise of them, that many brassfounders appear to be under the impression that all their troubles would disappear if they had an electric furnace suitable for brass melting. It may be of interest, therefore, to describe briefly the types of electric furnace now in use, and to consider the lines upon which developments are likely to proceed, and the prospects of success of the electric furnace for the melting of non-ferrous metals and alloys

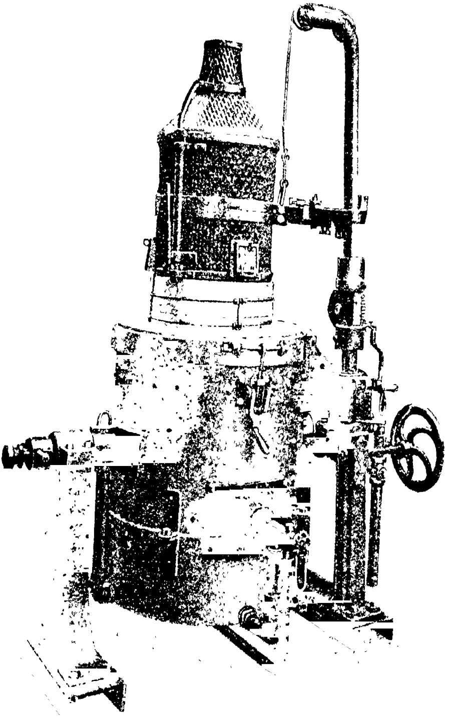


FIG. 8.—Buess Oil-fired Tilting Furnace.

The furnaces in use at the present time are usually divided into two classes, viz. (1) arc, or more correctly electrode, furnaces; and (2) induction furnaces.

Arc, or electrode furnaces, may, for the sake of convenience, be further divided into three groups. In the first of these, of which the Stassano furnace shown in fig. 9 is the most familiar example, three carbon electrodes enter the furnace at a slight inclination from the horizontal, and the bath of metal is heated by radiation from the arcs which are formed immediately above the surface, and which are directed downwards The heat is intense, but local, and the furnace is generally rotated in order to mix the metal and ensure homogeneity, although it is not certain whether this is actually necessary. The obvious weakness of this type of furnace lies in the excessive local heating of the upper part of the furnace, with consequent destruction of the roof, and also in the liability to fracture of the horizontal electrodes. In the

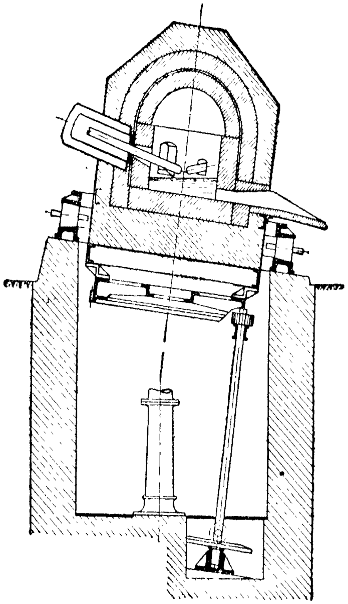


FIG 9 —Section of Stassano Electric Furnace.

second type of arc furnace, of which the best known representative is the Heroult furnace (shown in fig. 10), the carbon electrodes are arranged vertically and at some distance apart, so that the arc is formed between the surface of the bath and the electrode, the current passing through that part of the bath lying between the electrodes Owing to their size and vertical position, breakages are less liable to occur, and the electrodes themselves afford some protection to the roof from the intense heat of the

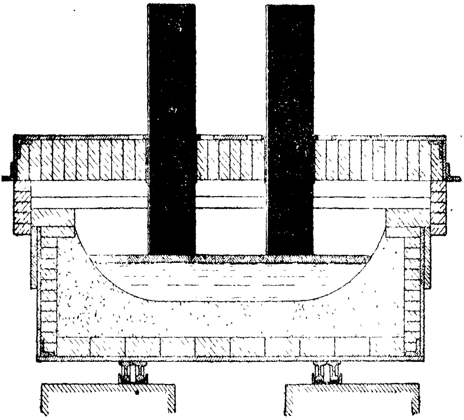


FIG 10.—Section of Heroult Electric Furnace.

arcs. The maximum heating effect is on the surface of the metal, and this is the ideal condition for a refining furnace in which the refining operation depends upon chemical reactions taking place between the slag and the metal. For example, in the refining of steel in which the object aimed at is the removal of sulphur, the intense heat of the electric arc enables a highly refractory slag containing as much as 60 per cent. of lime to be used, which readily combines with the sulphur in the steel with the formation of calcium sulphide. For the simple melting of metals, however, where no flux is used, the local heating of the arcs is a serious disadvantage.

In the third type of furnace, represented by the Girod furnace (fig. 11), the current enters the furnace by vertical carbon electrodes; but instead of leaving by similar electrodes as in the case of the Heroult furnace, it passes through the molten metal and leaves the furnace through water-cooled iron electrodes embedded in the bottom of the furnace.

The arc has been described as a necessary evil of the electrode type of furnace, and this is to some extent true, inasmuch as the heat is applied locally, and therefore at a very much higher temperature than is required. The aim of the designers of the more recent types of furnaces has therefore been to minimise the excessive heating of the arc and to apply a part of the heat to the metal by some other means. The Girod furnace, by reducing the number of surface arcs, was the first step in this direction, and the Nathusius furnace is the latest. This is circular in form, and has three carbon electrodes suspended vertically in the furnace, and three bottom electrodes of mild steel embedded in the hearth. Both top and bottom electrodes are arranged in the

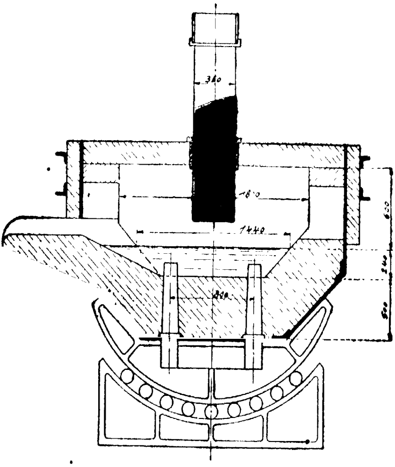


FIG. 11 – Section of Girod Electric Furnace.

form of a triangle, and the upper ones are so arranged that they can be drawn up when the furnace is tilted—a precaution which considerably diminishes the number of breakages. The current employed is a three-phase alternating, of any convenient frequency, and is supplied to the furnace through a step-down oil transformer which reduces the voltage of the mains to that of the furnace. Different systems of connection are employed, which need not be described in detail, but in each case the current is caused to flow not only between one upper electrode and another, or between one bottom electrode and another, but also between the upper and bottom electrodes. One system of connection is shown in fig. 12. Not only is the bath heated by the arcs on the surface, and by the passage of the current through it, but also by the heat generated in the bottom of the furnace due to the passage of the current between the bottom electrodes.

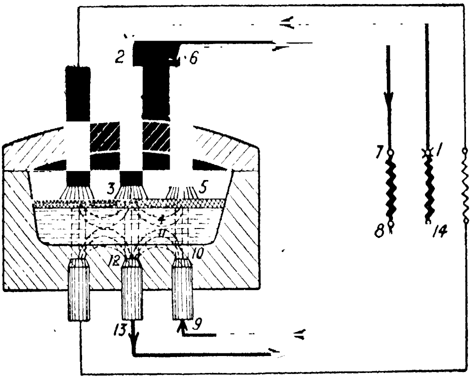


FIG. 12.—Connections in Nathusius Electric Furnace.

In spite of all efforts, however, the local heating of the arc is not eliminated, but only lessened, and at the expense of simplicity both in design of furnace and in electrical equipment.

Induction furnaces.—If a coil of copper wire through which an alternating current is passing is placed in position near a second coil, but without touching it, a current is "induced" in the second coil. The loss of power is small, and the respective currents may be varied at will, as they are inversely proportional to the number of turns in the windings. This is the principle of the transformer, by means of which it is possible to transform currents of low voltage to high voltage and *vice versa*. It is obvious that the secondary coil may consist of any ring of metal, and if such a ring is contained in an annular crucible or hearth, and the resistance of the current induced in it is sufficient to raise the temperature to the melting-point of the metal, then the transformer becomes an induction furnace.

From the electrical point of view the induction furnace is very much more efficient than the arc furnace, but from the metallurgical point of view it suffers from serious disadvantages quite apart from its high initial cost. In the first place, the annular shape of the crucible is far from ideal, especially where refining operations have to be carried out depending upon reactions between metal and slag. In the second place, the furnace can never be completely emptied. A cold charge does not form a sufficiently good conductor for the secondary current, and it is therefore necessary to leave a portion of the preceding charge in the furnace. This means that it is impossible to use the furnace for melting alloys of varying composition. In order to minimise the first of these disadvantages, the Rochling-Rodenhauser furnace has been built with two or three annular crucibles, instead of one as in the case of the Kjellin and Frick furnaces, which meet in the centre of the furnace, forming an open space in which the necessary operations can be carried out. The furnace is shown in section and plan in figs. 13 and 14.

From the foregoing brief description of the electric furnaces in use at the present time, it will be seen that furnaces of the arc type are essentially refining furnaces, in which the heat is communicated to the metal through a layer of slag. While this may be an ideal condition for such operations as the refining of steel, it is of no service in the melting of alloys, for which purpose the intense local heating of the arc is totally unfitted. On the other hand, the features of the induction furnace which have militated against its adoption in the manufacture of steel are of little or no importance in the melting of alloys, and it is to this type of furnace, or some modification of it in which the heat

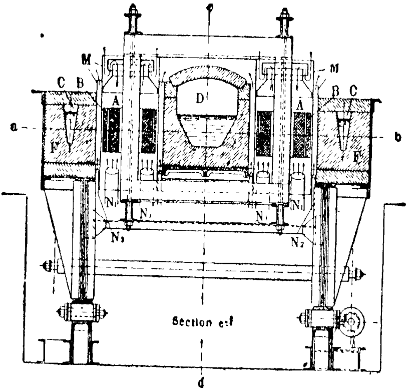


FIG. 13.—Section of Roehling-Rodenhauser Electric Furnace.

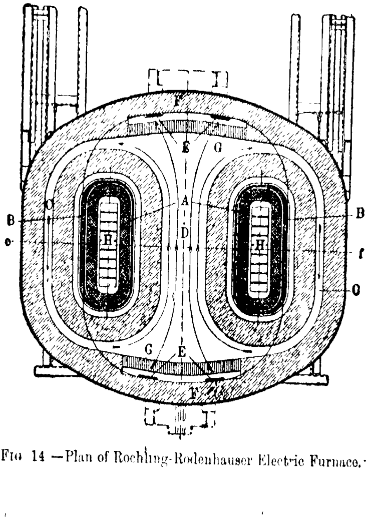


FIG 14 —Plan of Roehling-Rodenhauser Electric Furnace.

is developed in the metal itself by resistance to an electric current, that the manufacturer of alloys must look for the successful electric melting furnace.

It can, in fact, be claimed that the induction furnace is already being used for the melting, if not for the manufacture, of alloys; for in some of the Continental steel works it is being employed for melting ferro-manganese, as it is stated that considerable economies can be effected by the addition of ferro-manganese in the molten state to the bath of steel. Whether this is so or not, the fact that an alloy so readily oxidisable as ferro-manganese can be maintained in a molten condition for any length of time is sufficient proof of its adaptability to the melting of alloys. But most alloys possess a higher conductivity for electricity than ferro-manganese, and this is perhaps the weakest part of the induction furnace. In order to melt alloys which offer little resistance to the passage of electricity, very large currents must be employed to raise the temperature sufficiently to melt them

An ingenious furnace has been designed by Dr Carl Hering, in which he utilises one of the phenomena observed in the induction furnace, and known as the "pinch effect"

When an electric current flows through a molten conductor the electromagnetic forces coming into play cause it to contract in cross-section, and if one part of the conductor is already smaller in cross-section than the rest (a condition which frequently occurs in an induction furnace, due to the repairing of the crucible), and currents of large amperage are being employed, the contraction naturally takes place at this point and may lead to an actual rupture of the conductor and interruption of the current. This contraction of liquid conductors is the phenomenon known as the "pinch effect." As long as the conductor is not actually broken the pinch effect may be utilised to effect circulation of the metal. The contraction of the conductor causes the metal in the centre to flow, and, as the conductor is now smaller than the containing vessel, fresh metal flows in to fill up the space. Hence the motion takes place in one direction in the centre of the conductor, and in the opposite direction on the outside, as shown by the arrows in fig. 15. In the Hering furnace water-cooled electrodes are embedded in the furnace, and connection is maintained with the main mass of metal in the crucible by means of two narrow channels filled with the metal to be melted. It is in these channels that the heat is generated and from them the mass of metal in the crucible is kept in motion. Fig. 16 shows diagrammatically the main features of the Hering furnace, in this case adapted for bottom pouring. Owing to the small sectional area of the channels the metal in them is readily heated without the use of heavy currents. Moreover, as soon as the metal in the channels is melted the pinch effect causes the hot metal to be squirted into the crucible and its place taken by cooler metal, so that complete circulation and uniform heating of the metal in the crucible is ensured.

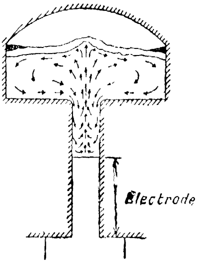


Fig. 15.—Circulation by "Pinch Effect"

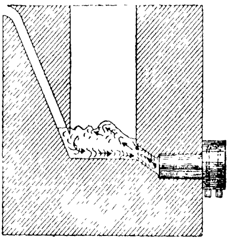


Fig. 16 Hering Furnace

It is too early to speak with any assurance as to the practical working of this furnace, but it certainly appears to combine the advantages of the arc and induction furnaces without their disadvantages. There is no excessive local heating as in the case of the arc furnace, the heat being generated in the metal itself as in the case of the induction furnace. Unlike the induction furnace, however, the transformer does not form a part of the furnace, where it is always liable to damage by hot metal, etc., but is completely detached. Further, the metal can be melted out of contact with air or furnace gases, so that oxidation troubles should be reduced to a minimum

As regards costs, the construction of the furnace is simple and the initial cost therefore low. The electrodes being of metal are cheap, and are not burnt away as in the case of carbon electrodes, which form such a serious item in the costs of arc furnaces.

Working costs are said to be low, and it is claimed that 10 kw.-hours are required to melt 1 cwt. of brass, or, taking the cost of current at ½d. per kw.-hour, 5d. per cwt.

In the manufacture of alloys on a large scale it is not always easy to produce a mixture of uniform composition even with careful stirring, and in practice it is often considered desirable, if not necessary, to re-melt the alloy a second time. The difficulty is greatest when the metals to be alloyed have widely different melting-points, and is still further increased if one of the metals is volatile. In order to reduce this difficulty to a minimum the pure metals are not melted together, but previously made alloys, whose composition is known, are used to make the final alloy. For example, in the case of German silver, which is composed of copper, nickel, and zinc, the zinc melts at 419° and the nickel at 1427°, and it is evident that if the three metals were placed in a crucible and raised to the necessary temperature most of the zinc would be lost by volatilisation before a uniform alloy was obtained. To overcome this difficulty German silver is made by melting together an alloy of copper and nickel, usually containing 50 per cent. of each metal, and brass. The copper-nickel alloy has a lower melting-point than pure nickel, while the brass has a higher melting-point than zinc, and the melting-points being thus more nearly alike the metals are more readily alloyed and the loss of zinc by volatilisation is very materially reduced. Another difficulty met with in melting metals to form alloys is the liability of the metals to become oxidised, and this subject is of such importance that it deserves some consideration. It is well known that some metals are capable of absorbing, dissolving, or alloying with considerable quantities of their oxides with most injurious results, but this behaviour of metals towards their oxides is of more common occurrence than is generally supposed. The influence of oxide on a molten metal may be readily seen by melting a small quantity of copper in a crucible without taking any precautions to prevent oxidation. The metal will be found to be moderately fluid, but if a small quantity of phosphor-copper is now added to the molten metal the increase in the fluidity of the metal is remarkable, and cannot fail to be noticed. For some time this increase in the fluidity of a metal was not properly understood in its practical applications, and when aluminium was first used as a deoxidiser for steel it was commonly stated that the effect of the aluminium was to lower the melting-point of the steel. Measurements of the melting-point, however, proved that there was no such lowering, but merely an increase in the fluidity, which was made more apparent by the heat produced by the combination of the oxygen with the aluminium.

In order to prevent oxidation as far as possible the metals are melted in graphite crucibles and covered with a layer of charcoal, resin, or other carbonaceous material. In some cases borax is used as a covering, as it melts easily and forms a protecting layer, while at the same time it combines with any metallic oxides present and keeps the molten metal clean. The alloy is stirred with a carbon stirrer, or in some cases with a green pole, the gases evolved from the wood serving to reduce any oxides present. In spite of these precautions, however, oxides are frequently formed which are not reduced by carbon, and the difficulty then presents itself of deoxidising the metal In order to effectually free a molten metal or alloy from oxide, it is necessary that the deoxidiser used shall have a stronger affinity for oxygen than the metal to be deoxidised, and, secondly, that any excess of the deoxidiser over that necessary to completely remove the oxide shall have no injurious effect upon the metal itself. A large number of deoxidisers are now manufactured, and the following list (p. 27) gives those most commonly used, together with the alloys for which they are most suitable and the form in which they are employed.

Boron is now being used as a deoxidiser for copper in the production of copper castings for electrical work Unlike the other deoxidisers, boron does not alloy with copper, so that the addition of a slight excess does not impair the electrical conductivity of the copper.

Deoxidisers should only be used to free the metal from the unavoidable oxidation which takes place even during the most careful melting, and should never be regarded as an infallible remedy for careless melting. The knowledge that oxidation can be partially or wholly cured should not hinder the strictest precautions being taken to prevent oxidation during melting. Excessive oxidation caused by too rapid melting and consequent overheating of the metal, or by overcharging the crucible, is often incompletely remedied by the addition of deoxidisers

Alloy	Deoxidiser.	Used in form of
Iron alloys	Manganese	Ferro-manganese and spiegeleisen
,, ,,	Silicon	Ferro-silicon and silicides.
,, ,,	Calcium	Ferro-calcium silicide
,, ,,	Aluminium	Aluminium and ferro-aluminium silicide
,, ,,	Titanium	Ferro-titanium
,, ,,	Vanadium	Ferro-vanadium.
Bronze	Phosphorus	Phosphor-copper and phosphor-tin.
,,	Aluminium	Aluminium.
,,	Silicon	Cupro-silicon.
,,	Zinc	Zinc
,,	Manganese	Cupro-manganese.
German silver	Magnesium	Magnesium or cupro magnesium
,, ,,	Calcium	Calcium-aluminium alloy
Silver-copper alloys	Cadmium	Cadmium
Aluminium alloys	Magnesium	Magnesium
,, ,,	Phosphorus	Phosphor-tin.

Pouring and Casting.—It has long been known that the temperature at which metals and alloys are poured has an important influence on their mechanical properties, and the most suitable casting temperature for any particular alloy has been determined entirely by practical experience. There is a lack of definite information on the subject, but Longmuir is responsible for some interesting observations and experiments which deserve attention. He cites the case of a number of cast-iron test pieces cast from a 5-ton ladle during an interval of fifteen minutes. Transverse tests on bars 2 ins by 1 in. placed on supports 3 ft. apart varied from 22 to 35 cwt

Another series of experiments on a special alloy, whose composition is not given, showed a tensile strength varying from 12·5 to 26·2 tons per sq. in., and corresponding elongations varying from 5·0 to 51·6 per cent. on a length of 6 ins. Two examples are also quoted of castings which failed to meet the required specification, but when broken up and re-melted, without any further addition of metal, and cast at a proper temperature, gave perfectly satisfactory results

Alloy	No.	Casting Tempera-ture.	Elastic Limit. Tons per sq. in.	Maximum Stress in Tons per sq. in.	Extension per cent. on 2 ins	Contraction of Area per cent.	Bending Angle in Degrees
Gunmetal	1	1173	6·468	8·376	5·5	4·23	30°, broken half through
	2	1069	8·482	14·838	14·5	16·71	40°; cracked.
	3	965	8·984	11·018	5·0	6·36	40°, ,,
Yellow brass	4	1182	4·432	11·484	37·75	31·405	Parallel over ¾-in. radius
	5	1020	3·974	12·713	43·00	35·66	,, ,, ,,
	6	850	4·150	7·447	15·00	15·25	,, ,, ,,
Red brass	7	1308	4·284	6·855	13·25	12·65	Parallel over ¼-in. radius badly cracked.
	8	1073	4·263	12·649	26·00	30·285	,, ,, ,, then hammered flat
	9	1058	4·376	5·670	5·5	6·64	105°; cracked
Muntz metal	10	1038	8·753	12·454	6·0	10·60	80°; broken.
	11	973	9·637	18·889	15·0	16·10	180°, unbroken.
	12	943	9·526	16·287	9·5	14·81	180°; broken
Cast iron	13	"Hot"	...	12·271	...	...	
	14	"Fair"	...	13·104	...	...	
	15	"Cold"	...	11·094	...	...	
Malleable iron	16	"Hot"	17·41	24·335	1·75		
	17	"Fair"	16·16	26·937	5·75	10·16	Broke in shoulder.
	18	"Cold"	12·24	24·02	3·50	6·24	,, ,, ,,

Longmuir has made a number of experimental castings with various alloys, and the figures in the foregoing table show his results. The figures explain themselves, and it is only necessary to add that the quantity of alloy melted was in every case over 50 lbs. in weight. Three bars were cast at a high temperature, and the metal allowed to cool in the crucible for a few minutes. A second set of three bars was then cast, followed after an interval by a third set of three, these last being cast at a temperature at which the metal would just flow.

If the alloy is cast at too high a temperature it possesses the coarse structure characteristic of a slowly cooled metal; whereas if it is poured at too low a temperature, not only is there risk of the alloy becoming partially solid, or the less fusible constituents separating out, before pouring, but also it solidifies immediately on coming in contact with the mould, with the result that there is a lack of cohesion in the ingot. Moreover, on account of the decrease in the fluidity of the alloy at temperatures only slightly above the melting point, it is liable to enclose scum, slag, or charcoal, which is unable to float to the surface. The result is an unsound ingot which cracks when rolled.

The proper temperature of casting would appear to be such that the mould is entirely filled with molten metal, which begins to solidify almost immediately after the pouring is completed. Determinations of the casting temperature of standard silver carried out at the Royal Mint showed that the average temperature was nearly 100° above the initial freezing-point of the alloy, or about 980°, and this would seem to be a suitable difference in temperature for alloys melting in the neighbourhood of 900°. In the case of alloys with much lower melting-points, which would cool more slowly, the difference between the melting-point and the casting temperature can with advantage be decreased. Thus with aluminium alloys such as magnalium, and alloys of lead and tin, the casting temperature should be only slightly higher than the initial freezing-point.

Closely connected with the casting temperature is the rate of cooling of the alloy, a matter of very great importance. Generally speaking, slow cooling produces a large grain, a coarse structure, and relatively weak alloys; while rapid cooling gives a fine structure and a stronger, but more brittle, alloy. The rate of cooling is to a great extent controlled by the temperature of the moulds. These are frequently heated in order to prevent too rapid cooling, and in some cases it has been found that the temperature of the moulds is of great importance in determining the quality of the alloy. An example of this occurs in the casting of certain antifriction alloys, which will be considered later.

Moulds.—Owing to the extended range of temperatures through which different alloys melt, a variety of materials are available for making moulds. Iron, brass, sand, plaster of Paris, and a number of other materials may be employed; but those most commonly used are iron and sand compositions. Alloys intended for rolling or drawing, such as steel, bronze, brass, German silver, magnalium, gold and silver alloys, etc., are cast in iron moulds; while those which are to be cast into objects of various shapes, merely requiring to be finished by turning or filing, are cast in sand moulds.

Iron moulds are made in two pieces, which are usually held together by clamps or by a ring and wedge device, intended to facilitate the removal of the ingot. The interior of the mould is either oiled, blackleaded, or smoked before the alloy is poured in. The foregoing remarks do not apply to ingot moulds used in casting steel, which are of special form and do not receive any oiling or other treatment previous to casting. They are made of grey hæmatite iron in the form of truncated pyramids of any desired section, with just sufficient tapering to allow the mould to be easily removed from the solid ingot. The second part of the mould, in this case, consists of a cast-iron bottom plate upon which the moulds stand.

The material used in making moulds for "sand castings" is a mixture of somewhat variable composition, but usually contains about 5 per cent. of clay, 1 to 2 per cent. of iron oxide, and the remainder of clean sand. Where fine castings with a specially good surface are required, the surface of the mould is "faced" with flour or a mixture of flour and charcoal.

The "pattern" round which the sand is moulded is usually made of hard wood, and is varnished or blackleaded to enable it to leave the sand easily. Allowance must also be made for the shrinkage of the metal on cooling. In casting alloys sharp corners or angles should be avoided, as far as possible, for a double reason. In the first place, such patterns are difficult to mould; and, in the second place, sharp angles give rise to a line of weakness in the casting which may result in fracture. This line of weakness is due to the fact that crystallisation takes place in a line at right angles to the face of the mould, and it follows that if two faces form a sharp angle the crystallisation starting from both faces will meet and produce a line of separation which bisects the angle. Prof. Turner states that a moderate internal pressure will frequently force out the bottom of a cylinder in a single piece if it has been cast with sharp corners. For this reason rounded curves should be adopted wherever possible.

After-treatment of Alloys.—When an alloy leaves the ingot mould it is subjected to a number of operations, all of which affect its properties to a greater or less degree. These operations may be described as (1) mechanical treatment such as rolling, drawing, spinning, etc.; (2) thermal treatment, such as annealing, chilling, tempering, etc., and (3) chemical treatment, which may be merely a cleaning of the surface by pickling in acid or alkali, or an actual alteration in the composition and character of the surface of the alloy by pickling or by cementation.

The influence of these operations will be considered separately.

1. Influence of Mechanical Treatment.—All metals are more or less compressible, and in the light of recent research it would appear that compressibility is a periodic property, and closely connected with, if not proportional to, the atomic volume. When subjected to mechanical treatment, such as rolling, hammering, or drawing, metals and alloys undergo compression and their mechanical properties are altered. The metal becomes stronger, harder, and more brittle, or, in other words, the tensile strength is increased and the elongation decreased. The practical application of alloys hardened by mechanical treatment may be seen, to take a single example, in the use of standard silver for the blades of dessert knives, fish knives, etc. These are manufactured by hammering, or, in the cheaper varieties, by "hard rolling." In the case of alloys experimental data are wanting; but it has been shown with pure metals that the greater the compressibility the more rapidly does it decrease with increasing pressure, and, according to Le Chatelier, the tensile strength of metals hardened to their maximum extent is almost exactly double their strength in their normal or softened condition. His figures for five metals are as follows.—

Metal.	Tensile Strength in Tons per sq. in.	
	Minimum Hardness.	Maximum Hardness.
Copper	15·87	32·38
Nickel	34·92	66·66
Aluminium . . .	7·62	15·87
Silver	11·43	24·12
Cadmium . .	1·58	3·17

As regards alloys, it is probable that those consisting of solid solutions which, as will be seen later, have structures similar to those of pure metals and are the only alloys capable of receiving much mechanical treatment without being previously heated, will behave in much the same way as pure metals. In some cases alloys are rolled while hot, and in others they are rolled cold. Cold rolling produces a greater degree of hardness than hot rolling, and the maximum hardness is produced by cold drawing to form wire or rod. The condition of maximum hardness, however, is not a stable one, and Le Chatelier has shown that a metal which has attained a state of maximum hardness becomes gradually softer in the course of time. Thus wires of silver and copper tested some hours after drawing showed a decrease in strength of 2 to 2·5 tons per square inch from those tested immediately after drawing. It is evident that this change, which Le Chatelier has aptly described as "spontaneous annealing," is of the utmost importance, and renders tests made on hardened metals of more than doubtful value. Moreover, Le Chatelier's work was carried out on very soft metals in which the effort of the metal to return to its normal condition merely produced a softening; but in the case of harder metals and alloys the results are very much more serious. The forces coming into play are so considerable that in the course of time the metal suffers deformation and in many cases actual fracture. This phenomenon is commonly known as "season cracking."

2. Influence of Thermal Treatment.—After being subjected to mechanical treatment metals and alloys are usually too hard and brittle to be of use, and it is necessary to soften them by reheating or annealing. This operation is usually carried out either in closed furnaces of the muffle type or in reverberatory furnaces (under reducing conditions) when the size of the pieces to be annealed does not permit of the use of a muffle furnace. Very small objects, such as pieces of standard silver to be used for jewellery, are sometimes annealed by simply resting them on the hot coke in the open furnace. Formerly the operation of annealing was carried out in the crudest manner, but within recent years the importance of the subject has been realised, with the result that annealing furnaces have been greatly improved, and it is now possible to carry out the process with practically no surface oxidation or alteration of the metal

From what has already been said with regard to "spontaneous annealing" it follows that there is no definite temperature above which a metal or alloy can be softened by annealing. The change takes place gradually but extremely slowly at normal temperatures; more rapidly as the temperature rises, until a temperature is reached at which the change takes place almost instantaneously. For practical purposes, however, there is a temperature for every metal and alloy below which annealing is impracticable on account of the length of time necessary for it to reach the required condition. The annealing of brass at different temperatures has been thoroughly investigated by Charpy, and his results are dealt with in the chapter on brass. More recently the subject has received the attention of Matweef and Rose. The latter has dealt specially with the annealing of coinage alloys, and has determined the temperatures at which softening begins to be perceptible in coinage blanks, together with the temperatures at which softening is completed in thirty minutes and in less than one minute His results are given in the following table (p. 34).

If a metal is annealed at too high a temperature its mechanical properties are injuriously affected, and it is then frequently described as "burnt" This word is somewhat loosely employed to describe any deterioration of mechanical properties due to annealing, and as such deterioration may be due to several causes it is necessary to distinguish between them.

Metal or Alloy.	Lowest Temperature observed at which Softening begins to be perceptible.	Temperature at which Softening is nearly completed.	
		In about half an hour.	In less than a minute.
Gold	80°	130°	200°
Silver	80	400	500
Copper	275	360	400
Nickel	300	700	...
Zinc	15	125	..
Aluminium, containing 2 per cent. iron	250	300–400	
Cadmium, possibly not pure	15	150	..
Gold-copper alloys—			
Au 916·6̇, Cu 83·3̇	290	500	600
Au 900, Cu 100	300	500	600
Silver-copper alloys—			
Ag 925, Cu 75	230	550	600
Ag 916·6̇, Cu 83·3̇	230	600	..
Ag 900, Cu 100	230	600	.
Ag 835, Cu 165	(?) 230	650	
Ag 800, Cu 200	300	700	700
Ag 719, Cu 281	300	700	.
Coinage bronze—			
Cu 95, Sn 4, Zn 1	200	470	600
Nickel-copper alloys—			
Ni 20, Cu 80	300	550	..
Ni 25, Cu 75	300	650	
Ni 30, Cu 70	300	600	
Ni 50, Cu 50	400	700	...

Annealing at too high a temperature may result in excessive crystallisation and even in a return to the structure of a cast metal. Such a change of structure is, however, not chemical but purely physical, and can be remedied by suitable heat treatment. Again, annealing at too high a temperature may cause segregation of one or more of the constituents of an alloy. A familiar example of this is to be found in the case of steel in which the carbide segregates between the crystals of iron. Photograph 46 shows a sample of steel which has been over-annealed in this way, but this structure can also be remedied by heat treatment, and the word "burnt" as applied to it is a misnomer. If, however, the steel is heated to a slightly higher temperature, actual oxidation or true burning occurs, and for this there is no remedy except remelting and deoxidation.

In the case of brass excessive annealing is accompanied by volatilisation of zinc. This in itself is not burning, but the subject is imperfectly understood and requires further investigation.

Annealing is usually followed by slow cooling, but in some cases rapid cooling produces a softer metal. Examples of this are to be found, in the case of pure metals, with silver; and in the case of alloys, with magnalium (see Chap. XIII.) The alteration produced by annealing requires time, and takes place more rapidly as the temperature is raised. On the other hand, impurities render the process of annealing slower.

The properties of some alloys are profoundly altered by chilling, quenching, or rapidly cooling from a high temperature. The object of such treatment is to fix or maintain, as far as possible, the structure possessed by the alloy at the temperature from which it is quenched, and it follows that the treatment is only applicable to alloys which undergo a transformation or molecular change on heating or cooling. It also follows that the effect produced by quenching will vary with different alloys. Steel, for example, is hardened by quenching, whereas the same treatment applied to bronze renders the alloy softer and more malleable, the rapid cooling preventing or hindering the formation of a hard constituent, which is always formed in a slowly cooled sample. The temperature from which the alloy is quenched depends upon the temperature at which the molecular transformation takes place, and must, of course, be above that temperature. The tendency of metals which have been cold worked to revert to their original condition has already been referred to, and the same tendency is always present in metals whose properties have been affected by sudden cooling. They are in a more or less unstable condition, and it sometimes happens that changes do actually take place. Such changes are usually described as "ageing." Examples of this are to be found in many of the alloys of aluminium which are softened by quenching but gradually recover their hardness.

The structure of an alloy can never be absolutely fixed by quenching, for the simple reason that the quenching can never be instantaneous and the efficiency of the quenching depends on the size, or, more strictly speaking, on the weight, specific heat, and conductivity of the alloy to be quenched; and also on the temperature and nature (and more especially the conductivity) of the bath in which the quenching takes place.

Quenching is usually carried out in water, solutions of salts in water, oils, lead, or the more fusible alloys of lead and tin.

Tempering consists in reheating a quenched alloy to a temperature below that from which it was quenched with the object of destroying the internal strain produced by the quenching, without affecting its molecular structure. The softening effect of this reheating is greater as the temperature is raised, but the temperature must be well below the point of transformation. A better example of the influence of heat treatment on the structure of an alloy could hardly be chosen than that given by Roberts-Austen and reproduced in photograph 1. The photographs all represent a steel containing 1·5 per cent. of carbon. The centre photograph shows the structure of the metal as it comes from the cementation furnace. No. 1 shows the structure after heating to 1000°, working and slowly cooling. In No. 2 the metal has been heated to 850° and cooled in air. In No. 3, instead of cooling in air, the metal has been quenched from the same temperature, 850°, in water. The steel is thus hardened and the pearlitic structure has been entirely replaced by martensite. In No. 4 the metal has been raised to a higher temperature, 1050°, and more rapidly cooled by quenching in iced brine. The structure now consists of bands of martensite, alternating with lighter and softer bands of austenite. If this metal is now cooled to the temperature liquid air the structure is profoundly altered as shown in No. 5 In No. 6 the steel has been quenched from a temperature near its melting-point, and the result is a "burnt" steel. The structure shown in No. 7 is the result of prolonged annealing at 650°. The cementite and pearlite are well defined. Lastly, No. 8 shows the original structure produced by heating any of the samples, except No. 6, to 850°, working, and slowly cooling.

Influence of Chemical Treatment.—After an alloy has been subjected to mechanical and thermal treatment it is necessary to remove the surface deposit of oxide which is formed on most alloys, and this cleaning is usually effected by "pickling" in an acid bath which is frequently heated. Now, this pickling has a decidedly prejudicial effect upon the mechanical properties of the alloy, and is so well recognised in the case of iron and steel that some specifications, including those demanded by the Admiralty, require that tests should be made upon the pickled metal. In the pickling of thin steel sheets intended for tin-plate manufacture, the decrease in strength and ductility of the metal is often accompanied by the formation of blisters on the surface; and in the pickling of hard steel rod containing about 0·8 per cent. of carbon the metal sometimes flies to pieces when immersed in the acid. The following figures by Baker and Lang illustrate the falling-off in the quality of steel rod by pickling. The first sample was pickled in a 38 per cent sulphuric acid bath for one hour, the second in an 11 per cent. bath for forty-five minutes, and the third in a 10 per cent. bath for one hour ten minutes, the temperature of the bath in each case being 100°.

	Tensile Strength in lbs. per sq. in.			Percentage Contraction.		
	1.	2.	3.	1.	2.	3.
Before pickling . .	65,700	59,700	69,100	63	66	67
After pickling . .	61,400	59,700	64,200	38	44	47

On reheating, the metal returns partially, but not entirely, to its former state.

There is no doubt that these results are due to the hydrogen, which is evolved in considerable quantity during the operation of pickling, and the action is more readily understood when we consider the following facts. Hydrogen at the normal temperature is easily capable of penetrating steel, and at 100° the penetration must take place more readily. Moreover, the action of the acid leaves a rough surface on the metal, which favours the penetration of the gas. Nascent hydrogen is a powerful reducing agent, and is capable of reducing metallic oxides, whether formed in the process of melting, or rolled into the metal during subsequent mechanical treatment, and the author has shown that this reduction can take place at a temperature of 100°. The reduction of oxides is accompanied by the formation of water, and the water being unable to pass out of the metal where the hydrogen entered, gives rise to an internal pressure, which may cause a blister in soft metal, a fracture in hard metal, or, at least, a falling-off in the mechanical properties. But at higher temperatures the action is reversed; metallic iron decomposes water vapour, and the hydrogen so formed is able to pass through the metal again.

The alteration in composition of an alloy due to pickling must not be overlooked. For example, in the case of standard silver, which in the hands of the silversmith undergoes repeated annealings and cleaning in acid, the copper is almost entirely removed from the surface of the alloy, leaving a coating of almost pure silver. This is a point which has to be considered by the assayer in taking an average sample of the metal. A change of composition in the surface layer of an alloy may also be produced by the ancient process of cementation. This process, which is still used in the hardening of steel, consists in heating the alloy, in the presence of a substance with which it is capable of alloying, at a temperature below its melting-point. Thus steel is superficially hardened by packing it in charcoal, and maintaining it at a high temperature for some time. The steel gradually alloys with the carbon, with the result that the surface is much harder than the interior. The same result is obtained by heating copper alloys in zinc dust, or even in zinc vapour, which alloys with the copper. A similar method is employed in the production of what is known as malleable cast iron; in this case the result aimed at is not the addition of a new element, but its extraction, cast iron being heated with oxide of iron, which decarburises the iron and renders castings softer and less brittle.

CHAPTER II.

PROPERTIES OF ALLOYS.

Density.—The density of an alloy is influenced (1) by the purity of the metals of which it is composed; (2) the mechanical treatment it has undergone; (3) the temperature at which it has been cast; and (4) the rate of cooling. These facts may to a great extent account for the disagreements shown in the work of Mallet, Calvert and Johnson, Matthiessen and Riche. Their work shows, however, that the density of an alloy is seldom the mean of the densities of its constituent metals, sometimes being greater and sometimes less than the mean. The mean density of an alloy may be calculated from the formula

$$M = \frac{(W + w)Dd}{Dw + dW},$$

where M is the mean density, W and w the weights of the constituent metals, and D and d their respective densities. The following alloys have frequently been given as examples of cases in which the densities are respectively greater and less than the mean:—

Alloys whose Density is less than the Mean of their Constituents.	Alloys whose Density is greater than the Mean of their Constituents.
Au and Zn	Au and Ag
Au ,, Sn	Au ,, Fe
Au ,, Bi	Au ,, Pb
Au ,, Sb	Au ,, Cu
Au ,, Co	Au ,, Ir
Ag ,, Zn	Au ,, Ni
Ag ,, Sn	Ag ,, Cu
Ag ,, Bi	Fe ,, Bi
Ag ,, Sb	Fe ,, Sb
Cu ,, Zn	Fe ,, Pb
Cu ,, Sn	Sn ,, Pb
Cu ,, Pd	Sn ,, Pd
Cu ,, Bi	Sn ,, Sb
Pb ,, Sb	Ni ,, As
Pt ,, Mo	Zn ,, Sb
Pd ,, Bi	

Matthiessen also states that some of the alloys of tin and gold have a greater and some a less density than the mean of their constituents, and the same is true of the alloys of bismuth and silver, and also of the alloys of some other metals.

Very little recent work has been done on the subject, and it appears that the study of the densities of alloys has been considered a barren field of investigation.

Colour of Alloys.—Of the well-known metals, only two—copper and gold—may be said to have any very decided colour; hence it might, at first sight, be supposed that the range of colour of alloys would be strictly limited. This, however, is not the case, and the colours produced in alloys are in many cases very remarkable and well worth a little consideration.

In the first place it is well known that the metals vary in their decolorizing power, and Ledebur has arranged the principal metals in the following order:—Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver and gold. Each metal in this series has a greater decolorizing action than the metal following it. For example, it requires nearly 50 per cent. of silver added to gold to produce a white alloy; whereas the addition of only 10 per cent. of aluminium is quite sufficient to completely destroy the colour of the gold. Again, an alloy of 75 per cent. of copper and 25 per cent. of zinc has the well-known colour of brass; but if the zinc is replaced by the same quantity of nickel, we get the perfectly white alloy so largely used for the Continental nickel coinage.

In addition to this property of destroying the colour of metals we have cases in which by the simple fusion of two metals the most unexpected colours are obtained. Thus an alloy of copper and antimony containing 51 per cent. of copper and 49 per cent. of antimony has a beautiful violet colour, and even more interesting is the case of the violet alloy of Roberts-Austen, produced by melting 78 parts of gold with 22 of aluminium.

In these cases we start with one coloured constituent, but it is possible to obtain coloured alloys even from two white metals. The alloy of platinum and aluminium, for example, containing 75 per cent. of platinum and 25 per cent. of aluminum, is distinctly yellow, and resembles gold containing a small percentage of silver. Another yellow alloy is obtained by the fusion of 33 per cent. of aluminium and 66 per cent. of cobalt.

Heycock and Neville have drawn attention to the alloy in the silver-zinc series corresponding to the formula AgZn, which is capable of assuming a red colour when heated to about 300° and suddenly chilled; and it has also been shown that the corresponding cadmium alloy AgCd has a distinct and very beautiful pink colour.

All these alloys are formed by the union of definite atomic proportions of their constituents, and must be regarded rather as chemical compounds than as simple metallic mixtures. They are perfectly homogeneous, brittle alloys, breaking with a conchoidal fracture; properties which render them practically useless to the art-metal worker. There are, however, a large number of useful, if less brilliantly coloured, alloys for the metal worker to choose from, and an excellent example may be found in the numerous gold alloys employed by jewellers and goldsmiths. Some of these, with their percentage compositions, are shown in the following table:—

Colour.	Composition.				
	Gold.	Silver.	Copper.	Iron.	Cadmium.
Deep yellow .	90		10	...	...
" .	53	25	22	...	...
Red . .	75	...	25	...	...
Dark red .	50	...	50	...	...
" .	25	...	75		...
Pale yellow .	91·6	8·3	...	...	...
" .	91·6		...	8·3	
Green . .	75	25	...	...	...
" . .	75	16·6	...	...	8·4
" . .	74·6	11·4	9·7	...	4·3
" . .	75	12·5		...	12·5
Grey . .	85·7	8·6	...	5·7	...
" . .	83·3	...	...	16·7	...
Blue . .	75	...	...	25	...
" . .	66·7	...	...	33·3	...

The coloured alloys used by the Japanese in their famous art-metal work have been described by Roberts-Austen and others, but a brief description of them may be of interest. The most important of these alloys are known as *shaku-do* and *shibu-ichi*, and both of them are, within certain limits, very variable in composition. Two samples of *shaku-do*, for example, gave the following analysis:—

Copper	94·50	95·77
Silver	1·55	0·08
Gold	3·73	4·16
Lead	0·11	...
Iron and arsenic	Traces	...

Other samples have been found to contain as little as 1·5 per cent of gold, but the precious metal is an essential constituent of the alloy and enables the metal to assume a beautiful surface colouring, or "patina," when treated with suitable pickling solutions.

Shibu-ichi is a copper silver alloy, and is fairly represented by the following analysis:—

Copper	67·31	51·10
Silver	32·07	48·93
Gold	Traces	0·12
Iron	0·52	...

In addition to these alloys and their various combinations one with another there are varieties of impure copper, all of which are capable of assuming different colours on pickling. The pickling solutions most commonly used are made up of the following ingredients, and are used boiling:—

	I.	II.	III.
Verdigris	438 grains	87 grains	220 grains
Sulphate of copper	292 ,,	437 ,,	540 ,,
Nitre	...	87 ,,	...
Common salt	...	146 ,,	...
Sulphur	...	233 ,,	...
Vinegar		1 gallon	5 drachms
Water	1 gallon	...	1 gallon

Examples of the different colours obtained by pickling may be seen at the Victoria and Albert Museum, South Kensington, where there is a collection of fifty-seven plaques illustrating the different sorts of bronze used in Japan. Another excellent collection, consisting of twenty four plates, is to be found in the Museum of Practical Geology in Jermyn Street.

In connection with the use of coloured alloys in art metal work a brief reference to the Japanese *mokumé* ("wood grain") and *mizu-nagashi* may not be out of place. An effect closely resembling the grain in wood is produced by taking thin sheets of various metals and alloys, such as gold, silver, *shakudo*, *shibu-ichi*, etc., soldering them together, and then either cutting a device into them and hammering the whole until flat, or else hammering from behind and then filing down the prominences. The methods are sufficiently well shown in the two illustrations (figs. 17 and 18). Fig. 18 shows the effect of these banded alloys in a bead which is only three quarters of an inch in diameter.

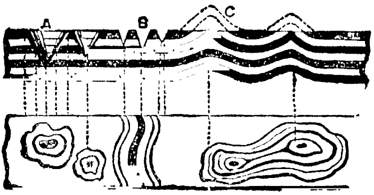


FIG. 17. Japanese Art Metal Work

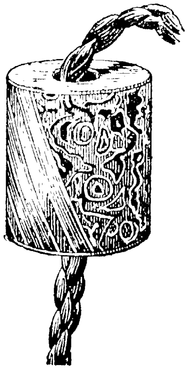


FIG. 18.—Japanese Art-Metal Bead

Specific Heat.—The most important determinations of the specific heats of alloys were made by Regnault in 1841. For the purpose of his investigations he divided alloys into two classes: those having a fusing-point considerably above 100° C., and those fusing at or near 100° C. In the case of the first class he concluded that the specific heat was an additive property, and agreed closely with the calculated specific heat obtained by multiplying the specific heat of each constituent metal by the percentage amount of the metal contained in the alloy and dividing the sum of the products by 100. This led him to announce that "the specific heat of the alloys at temperatures considerably removed from their fusing-points is exactly the mean of the specific heats of the metals which compose them." He further discovered that in the case of these alloys the product of the specific heat of the alloy into its atomic weight is approximately constant. In the whole series examined by him this number only varied from 40·76 to 42·05. On examining the second class of alloys, those which fuse at or near 100° C., Regnault discovered that they did not obey his law, and that the specific heats were in all cases higher than those obtained by calculation from the specific heats of the constituents. Moreover, he found that the product of the specific heats into the atomic weights varied from 45·83 to 72·97. Regnault's conclusions have been confirmed by Schimpff, who finds that, with the exception of magnesium and antimony, the specific heats of alloys agree very closely with the calculated figures. In the case of the magnesium alloys the figures are somewhat smaller than the calculated results, while those obtained from the antimony alloys are slightly higher. On the other hand, Saposhnikoff confirms Regnault's conclusions but does not mention the exceptions noted by Schimpff, although he has specially studied the antimony alloys.

Malleability has been described as the property which enables metals to be permanently extended in all directions, without rupture, by pressure produced by slow stress or by impact. The degree of malleability of a metal is measured by the ease with which its shape or form can be modified by rolling or hammering. The order of malleability of the common metals is as follows:—Gold, silver, copper, tin, platinum, lead, zinc, iron and nickel. Some metals are less malleable when hot than when cold and are described as *red short,* while those that are more malleable when hot are called *cold short.* Alloys are less malleable than pure metals, and the most malleable alloys are those whose structure most closely resembles that of pure metals.

Ductility is the property which enables metals to be permanently elongated, *i.e.* to be drawn into wire. The order of ductility of the common metals is as follows:—Gold, silver, platinum, iron, nickel, copper, zinc, tin, lead. Alloys are less ductile than pure metals, and, as in the case of malleability, the most ductile alloys are those possessing structures resembling pure metals.

The **hardness** of metals is measured in several ways. Bottone measured the hardness of metals by determining the time necessary to produce a cut of definite depth. Taking the diamond as 3010, the relative hardness of a number of metals was determined as follows:—

Manganese	1456	Gold	979
Cobalt	1450	Aluminium	821
Nickel	1410	Cadmium	760
Iron	1375	Magnesium	726
Copper	1360	Tin	651
Paladium	1200	Lead	570
Platinum	1107	Thallium	565
Zinc	1077	Calcium	405
Silver	990	Sodium	400
Iridium	984	Potassium	230

In the sclerometer, as devised by Prof. Turner, a cutting method is also employed, but in this case the hardness is measured by the pressure which must be applied to a diamond point in order to produce a scratch equivalent to a standard scratch on a standard metal surface.

Brinell measures the hardness of metals by determining the depth of the indentation produced by a hard sphere of known dimensions under a definite pressure This method is the one generally adopted in engineering practice.

In an ingenious little instrument invented by Shore, and known as the scleroscope, the hardness of a metal is measured by the height of rebound of a small hammer which is dropped from a known height through a graduated glass tube on to the surface of the metal to be tested.

It is obvious that the word "hardness" is used to describe different properties, and that the methods employed to determine the hardness of metals do not measure the same kind of hardness. Resistance to abrasion as measured by the sclerometer is not necessarily the same thing as resistance to crushing as measured by the Brinell method; nor do we know definitely the relation of either of these to the "resilience" as measured by the scleroscope In any case, however, it may be considered as a general rule that the hardness of a metal as measured by any of the above methods is increased by the addition of another metal.

Thermal Conductivity.—The power of alloys to conduct heat has been examined by several experimenters; but it was not until 858 that the subject was thoroughly dealt with by Calvert and ohnson, who made a large number of determinations, using alloys repared from pure metals. The apparatus employed consisted of a box containing a known volume of water; to this box one end of the bar to be tested was secured. The other end of the bar was maintained at a temperature of 90° C., and the relative conductivity of the bar determined by noting the rise in temperature in a given time of the known volume of water in the box. The conductivity of silver, which is the best conductor, was taken as 1000.

Calvert and Johnson state that in some cases the conductivity of an alloy is the mean of the conductivities of its constituent metals; but in many cases there appears to be no relation between the two. For example, the conductivity of silver was taken as 1000 and that of gold 981, but the conductivity of gold containing 1 per cent. of silver was found to be only 840.

These experimenters divide alloys into three classes according to their conductivity:—

1. Alloys which conduct heat in ratio with the relative equivalents of the metals composing them: alloys of tin and zinc, and of tin and lead.

2. Alloys in which there is an excess of equivalents of the worse conducting metal over the number of equivalents of the better conductor, such as alloys composed of one equivalent of copper and two of tin, or one of copper and three of tin, and which possess the remarkable property of conducting heat as if they contained none of the better conductor. The conducting power of these alloys is the same as if the bar were composed entirely of the worse conductor. Similarly in the case of the bismuth-lead alloys, those containing two equivalents of bismuth and one of lead, three of bismuth and one of lead, and four of bismuth and one of lead, all conduct alike, the decrease in the quantity of lead having no influence on the conductivity.

3. Alloys composed of the same metals as the last class, but in which the number of equivalents of the better conducting metal is greater than the number of equivalents of the worse conductor. In these alloys the conductivity tends towards the better conductor.

Matthiessen gives it as his opinion that the conductivity of an alloy furnishes no evidences of whether an alloy is a chemical compound or a mixture.

Electrical Conductivity.—The study of the electrical conductivity of alloys may be said to have begun with the publication, in 1860, of the results of Matthiessen's famous research. With regard to the conducting power for electricity he divides the metals into two classes :—

Class A.—Those metals which, when alloyed with one another, conduct electricity in the ratio of their relative volumes.

Class B.—Those metals which, when alloyed with one of the metals belonging to Class A, or with one another, do *not* conduct electricity in the ratio of their relative volumes, but always in a lower degree than the mean of their volumes. To Class A belong lead, tin, zinc, and cadmium. To Class B belong bismuth, mercury, antimony, platinum, palladium, iron, aluminium, gold, copper, silver, and "in all probability most of the other metals."

Matthiessen showed that the electrical conductivity of any series of alloys composed of two simple metals may be represented graphically by one or other of three typical curves which are respectively straight lines, L-shaped, or U-shaped. The metals of Class A produce alloys whose conductivity is represented by straight lines; those of Class A with Class B by L-shaped curves; and those of Class B with one another by U-shaped curves (see Chap. XVI.).

At the conclusion of a research which Roberts-Austen has justly described as classical, Matthiessen considers the nature of alloys and sums up his arguments in the following manner :—

"The question now arises, What are alloys? Are they chemical combinations, or a solution of one metal in another, or mechanical mixtures? And to what is the rapid decrement in the conducting power in many cases due? To the first of these questions I think we may answer, that most alloys are merely a solution of one metal in the other; that only in a few cases may we assume chemical combination—for example, in some of the gold-tin and gold-lead alloys; and we may regard as mechanical mixtures some of the silver-copper and bismuth-zinc alloys. The reasons for the foregoing assumptions are the following :—

"1. That if we had to deal with chemical combinations we should not find in the conducting power of alloys that regularity in the curves which certainly exists; for on looking at those belonging to the different classes we see at a glance that each class of alloys has a curve of a distinct and separate form. Thus, for the first, we have nearly a straight line; for the second, the conducting power always decreases rapidly on the side of the metal belonging to Class B, and then, turning, goes almost in a straight line to the side of the metal belonging to Class A. For the third group, we find a rapid decrement on both sides of the curve, and the turning-points united by almost a straight line.

"If we now examine the part of the curve where the rapid decrement takes place we find that in the lead and tin alloys it generally requires twice as much of the former as it does of the latter to reduce a metal belonging to Class B to a certain conducting power; for instance, to reduce that of silver to 67 it would require 0·9 vol. per cent. of lead, or about 0 5 vol per cent. of tin; to reduce it to 47·6 there would be required 1·4 vol. per cent. of lead, or about 0·7 vol. per cent. of tin. Again, to reduce bismuth to 0·261 there is required 1·4 vol. per cent. of lead, or 0·62 vol. per cent. of tin; and to reduce it to the minimum point of the curve, which is when alloyed with lead 0 255, and 0 215 when alloyed with tin, it requires 1·76 vol. per cent. of lead and 0·85 vol. per cent. of tin.

"2. We cannot explain the reason of the decrement of the conducting powers by assuming that the turning points of the curves are chemical combinations, for it is not at all probable that there are such as contain only 0 6 per cent of tin and 99·4 per cent. of bismuth; or 2 per cent of lead and 98 per cent. of bismuth; or 2·6 per cent of tin and 97 4 per cent. of silver.

"3. That the alloys at these turning points have their calculated specific gravities.

"From the similarity of the curves of alloys, where we may assume, from their chemical behaviour, that we have only a solution of one metal in another, we may always draw approximately the curve of the alloys of any two metals, if we know to which class they belong. Thus, before a single copper-gold alloy had been determined, the curve was almost correctly drawn, and agreed with that which was afterwards found by experiment."

"That some alloys are chemical combinations," he adds, "may be deduced from the following facts:—

"1. At the turning-points of the curve we generally find the alloys contract or expand.

"2. There is no regular form of curve (gold-tin, gold-lead, and silver-copper), so that it cannot be *a priori* even approximately represented.

"3. At the turning-points the alloys contain large percentages of each other.

"4. At the turning-points of the curves the alloys are different from each other in appearance (crystalline form, etc.)."

To the second question, "To what is the rapid decrement of the conductivity due?" Matthiessen says, "The only answer which I can at present give to this question is that most of the other physical properties of the metal are altered in a like manner."

In a later research Matthiessen determined the electrical conductivity of a large number of alloys and established formulæ by which the conductivity of an alloy at any temperature might be calculated.

More recently Le Chatelier, working with greater ranges of temperature, has shown that in the case of metals which do not undergo any molecular change at temperatures below their melting-points the increase of electrical resistance is proportional to the temperature. Many metals, however, such as iron, exhibit irregularities in the resistances which occur at definite temperatures, and are evidently due to molecular or allotropic changes in the metal. Similar changes are also shown in the case of alloys.

The electrical resistance of metals and alloys at very low temperatures has been studied by Dewar and Fleming, who have shown that in the case of pure metals the resistance decreases with the fall in temperature, and the evidence tends to show that at the absolute zero all the metals would be practically perfect conductors. In the case of alloys, however, the results are entirely different. The resistance decreases only slightly as the temperature falls, and in many cases the resistance at − 200° is almost as great as at 100°. The figures obtained by Dewar and Fleming for a number of alloys and metals are given in the following tables :—

ALLOYS.

Arranged according to Decreasing Resistance.

Alloy.		Specific Resistance in Microhms per c.c			Temperature Coefficient at 18° C
		At Boiling Water Temperature, 100° C.	At Normal Temperature, 18° C	At Liquid Air Temperature, −182° C	
Manganese steel	Mn 12%	75·29	68·52	55·41	0·00127
Manganin	Mn 12%, Ni 4%, Cu 84%	47·[illegible]	47·64	45·82	0·0[illegible]
Platinoid		42·88	41·9[illegible]	39·19	0·00031
Nickel steel	Ni 4·35%	[illegible]	30·40	19·47	[illegible]
Platinum, Iridium	Pt 80%, Ir 20%	27	31·[illegible]	26·03	[illegible]
Platinum, Silver	Pt 33%, Ag 6[illegible]	32·30	31·73	30·17	0·000243
German silver		30·7[illegible]	30·11	28·32	0·00273
Platinum, Rhodium	Pt 90%, Rd 10%	[illegible]	[illegible]	15·1[illegible]	0·001[illegible]
Copper, Nickel, Aluminium	Cu 87%, Ni 6·5%, Al 6·5%	15·78	15·[illegible]7	13·65	0·00[illegible]47
Copper, Aluminium	Cu 97%, Al 3%	9·57	[illegible]	7·[illegible]3	0·00[illegible]7
Gold, Silver	Au 90%, Ag 10%	7·00	6·42	4·82	0·00124
Aluminium, Silver	Al 94%, Ag 6%	5·09	4·[illegible]2	2·48	0·00[illegible]8
Titanium, Aluminium		4·94	4·08	1·66	0·00290
Aluminium, Copper	Al 94%, Cu 6%	3·97	3·09	0·72	0·00381
Silverine	Ni 17%, Cu 77%, Co 2%, Zn 2%, Fe 2%	2·61	2·17	0·91	0·00285

METALS.

Arranged according to Decreasing Resistance

Metal	Specific Resistance in Microhms per c.c.			Temperature Coefficient at 15° C.
	At Boiling Water Temperature, 100° C.	At Normal Temperature, 15° C.	At Liquid Air Temperature, −185° C.	
Lead . .	27·97	21·96	6·03	0·00411
Thallium . . .	24·66	18·75	4·89	0·00398
Nickel . .	19·42	14·65	1·91	0·00622
Tin	18·30	13·14	3·40	0·00440
"A" Iron (Armstrong's)	15·73	11·50	2·31	0·00514
Platinum . .	14·81	11·65	3·21	0·003520
"H.W." Iron (Hopkins and Williams)	14·63	10·01	1·22	...
Cadmium . .	13·84	10·98	2·95	0·00419
Palladium . . .	13·79	10·83	2·78	0·00354
Zinc . .	7·91	6·21	1·50	0·00406
Magnesium . .	5·99	4·65	1·00	0·00381
Aluminium . .	3·57	2·77	0·56	0·00423
Gold . . .	2·94	2·21	0·68	0·00377
Copper . . .	2·22	1·68	0·29	0·00428
Silver . .	2·06	1·57	0·39	0·00400

Lord Rayleigh suggests a possible explanation for the remarkable difference in the behaviour of alloys and pure metals, with regard to their electrical resistance, on the assumption of the heterogeneity of the alloys. According to this view, when a current is passed through an alloy, it sets up between the particles of the different metals a series of Peltier effects proportional to the current, and these create an opposing electromotive force also proportional to the current and indistinguishable, as far as experiments are concerned, from a resistance. If the alloy were a true chemical compound this opposing force would not exist.

This explanation is undoubtedly of great service in considering heterogeneous alloys, but it must be remembered that, in the case of the most perfectly homogeneous alloys known, namely, those of gold and silver, the alloy containing atomic proportions of the two metals and corresponding to the formula AuAg has the highest resistance of the series, a fact which can only be explained by assuming, as has been suggested, that the Peltier effects occur between the molecules themselves.

The variations in the electrical resistance of amalgams at different temperatures have been investigated by Mr R. S. Willows. The amalgams experimented upon include those of tin, zinc, cadmium, and magnesium; but the most interesting of these is the amalgam with zinc. For a given amalgam two curves could be obtained which differed entirely in certain important characteristics Thus, for example, if, after determining the resistance, the amalgam was heated and allowed to cool and the resistance again determined, it was found that it was greater after heating than before. This could be repeated several times, the increase in the resistance becoming less and less, until after heating about six times it was found that a further heating did not increase the resistance. When this condition was reached the resistances at various temperatures were determined and the results plotted in the form of a curve. The amalgam was then allowed to stand at the temperature of the room for several weeks, its resistance being measured every morning at the same temperature. It was found that the resistance gradually fell slowly for the first three days, most rapidly about the seventh, and then again more slowly. In some cases it took six weeks for the resistance to become steady. A second series of determinations were then made, when it was found that the curve so obtained differed entirely from the first.

Many attempts have been made to trace analogies between metallic conduction and the electrolytic dissociation of salt solutions, but so far without success. In 1861 Gérardin conducted some experiments on sodium amalgam, from which he concluded that the metals might be separated by means of an electric current; but Dr Obach, who repeated his experiments with great care, was unable to obtain any evidence of dissociation of the amalgam. In 1887 the question was again investigated by Roberts-Austen at the request of the Electrolysis Committee of the British Association. He experimented upon alloys of gold and lead and silver and lead placed in cavities cut in a fire-brick and maintained in a molten state, but was unable to detect any separation with currents of 300 amperes. It must be remembered, however, that at the high temperatures employed in these experiments the diffusion must have been very rapid, and would probably be more than sufficient to counterbalance any separation of the metals due to the electric current. With reference to these experiments it has been suggested by Professor Lodge that there must be a group of bodies on the borderland between alloys proper and electrolytes, in which some gradual change from wholly metallic to wholly electrolytic conduction might be expected.

Diffusion.—It has long been known that gases which do not act chemically upon one another are capable of mixing uniformly or diffusing into one another, even if the vessels containing them are only connected by a narrow tube, and if the vessel containing the lighter gas is placed above that containing the heavier gas. The same property of diffusion is observed in liquids, and becomes an important factor in the manufacture of alloys. It is evident, for example, that mere mechanical mixing could hardly produce the uniformity which is found in the alloy of gold and copper used for purposes of coinage. In this case 1200 ozs. of the alloy, containing 1100 ozs. of gold and 100 ozs. of copper, are melted at one time and cast into bars, when it is found that an assay of the last bar is practically identical with that of the first.

The question of the diffusion of metals was taken up by Roberts-Austen as a continuation of the work of Graham on gases and liquids, and in 1896 he communicated to the Royal Society the results of his investigations on the diffusion of gold and platinum in lead. In these experiments the molten metal was contained in tubes placed in an air bath, which was maintained at definite temperatures. The extent to which diffusion had taken place was determined by allowing the metal in the tube to solidify after a given time and analysing sections cut from the bar. The linear diffusion is expressed, in accordance with Fick's law, by the equation

$$\frac{dv}{dt} = k\frac{d^2v}{dx^2},$$

where x is the distance in the direction in which diffusion takes place, v is the degree of concentration of the diffusing metal, and t is the time. k is the diffusion constant, and is the quantity of metal in grams diffusing through unit area (one sq. cm.) in unit time (one day), when unit difference of concentration (in grams per c.c.) is maintained between the two sides of a layer 1 cm. thick.

Fig. 19 is the diagram given by Roberts-Austen to show the relative diffusion of gold and platinum taking place in a period of twenty-four hours in molten lead at a temperature of 500° C. The columns A B represent the actual length and diameter of columns of fluid lead, and the spheres represent the sizes of the buttons of gold and platinum extracted from the sections of the columns as shown. The curves are plotted with distances of diffusion as ordinates, and concentrations as abscissæ.

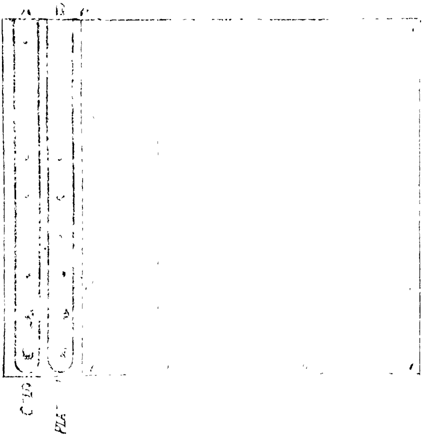


FIG. 19.—Diffusion of Gold and Platinum in Lead.

The determinations of *k* for a few metals are given in the following table:—

Diffusing Metal	Solvent	Temperature	*k* in square centimetres.	
			Per day	Per second.
Gold . .	Lead .	492°	3·00	$3·47 \times 10^{-5}$
,,	,, .	492	3·07	3·55 × ,,
Platinum . .	,, .	492	1·69	1·96 × ,,
,, .	,, .	492	1·69	1·96 × ,,
Gold .	,,	555	3·19	3·69 × ,,
,, .	Bismuth .	555	4·52	5·23 × ,,
,, .	Tin .	555	4·65	5·38 × ,,
Silver . .	,, . .	555	4·14	4·79 × ,,
Lead .	,, . .	555	3·18	3·68 × ,,
Gold . .	Lead . .	550	3·18	3·69 × ,,
Rhodium . .	,, . .	550	3·03	3·51 × ,,

By way of comparison with these figures the results of some determinations of the diffusion of metals in mercury published by Dr Guthrie in 1883 have been calculated by the same method and give the following values of k in sq. cms. per day :—

Tin in mercury at about 15°	.	.	1·22
Lead ,, ,,	.	.	1·00
Zinc ,, ,,	.	.	1·00
Sodium ,, ,,	.	.	0·45
Potassium ,, ,,	.	.	0·40

These results have since been practically confirmed by Humphreys.

Diffusion of Solid Metals. It has long been known that solid bodies are capable of diffusing into one another, and the old processes of cementation are based upon this fact; but it is only within comparatively recent years that the subject has received serious attention from a theoretical point of view. In 1820 Faraday and Stodart, while experimenting on the alloys of iron, observed that steel and platinum in the form of bundles of wire could be readily welded at a temperature considerably below that at which either of the metals alone would be affected. They further observed that on etching the welded mass with acid the iron appeared to be alloyed with the platinum. More than half a century later (in 1877) Chernoff drew attention to the fact that if two surfaces of iron are heated to about 650° in intimate contact with one another they will unite. From this date the publication of researches on the diffusion of solids became more frequent. In 1882 Spring demonstrated that alloys may be produced by compression of their constituent metals in a fine state of division, while Hallock in 1888 showed that similar results could be obtained without the aid of pressure, but at somewhat higher temperatures. In 1894 Spring showed that two carefully prepared surfaces of two metals pressed together and maintained at temperatures of from 180° to 400° for eight hours would interpenetrate and form alloys at the junction of the two metals. The first actual measurements of the rate of diffusion of solids are, however, due to Roberts-Austen, who extended his researches on diffusion from the fluid to the solid state, and in 1896 published the results of what is now justly considered one of the classical researches on alloys. He determined the rate of diffusion, *k*, of gold in solid lead at various temperatures, and his results are given below, with the rate of diffusion of gold in fluid lead at 550° for the sake of comparison :—

		K
Diffusivity of gold in fluid lead at	550° . . .	8 19
,, ,, solid lead	251° . . .	0·03
,, ,, ,,	200° . . .	0·007
,, ,, ,,	165° . .	0·004
,, ,, ,,	100° . . .	0 00002

In order to determine the rate of diffusion of gold in lead a the ordinary temperature, discs of pure gold were clamped to the ends of cylinders of lead ·88 cm. in diameter, and these were kept at the ordinary temperature of the atmosphere for a period of four years. At the end of this time it was found that the discs of gold adhered to the lead cylinders and that diffusion had taken place. Slices were cut off the cylinders, the first 0·75 mm. thick, and succeeding layers 2 3 mm. thick, and these were then assayed. The first layer was found to contain as much as 1 oz. 6 dwts. of gold per ton, while the fourth layer was estimated to contain 1½ dwt. per ton. From these results Roberts-Austen calculated that the amount of gold which would diffuse in solid lead at the ordinary temperature in one thousand years would be almost the same as that which would diffuse in molten lead in one day.

Liquation.—When two or more metals are melted together and allowed to cool it seldom happens that the resulting alloy solidifies, or freezes, as a whole and at a definite temperature. Usually one portion freezes first, rejecting another portion of different composition, which then solidifies at a lower temperature. This property is known as *liquation*, and has been made use of in the well-known Pattinson process for the separation of silver from lead. In this process it will be remembered that the lead containing silver is melted and allowed to cool slowly, the almost pure lead being ladled off as it solidifies, leaving a still molten alloy comparatively rich in silver.

The property of liquation has been long known, but it is to Dr Guthrie that we owe the first systematic investigation of the problem. He considers that the solidification of a molten alloy is analogous to the solidification of a mass of molten rock in which the quartz and felspar solidify before the mica. So, in the case of alloys, a certain metal or alloy solidifies first and eventually leaves behind the most fusible alloy of the series. This alloy Dr Guthrie calls the *eutectic* alloy. The constituent metals in the eutectic alloy do not occur in atomic proportions, and he remarks that "the preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, that it must be a chemical compound, seems to have misled previous investigators." He admits the existence of compounds, but declares that "the constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties less definite."

The phenomenon of liquation has been long known in the case of the copper-silver alloys, and, owing to the importance of these alloys for coining purposes, they have received considerable attention. D'Arcet in 1824 and Mercklein in 1834 both pointed out that the alloys of silver and copper are not homogeneous; and Levol, in 1854, as the result of a very careful investigation conducted on these alloys cast in both cubical and spherical moulds, came to the conclusion that the only homogeneous alloy of the series was that containing 71·89 per cent. of silver, which he considered to be a definite combination of the two metals corresponding to the formula Ag_3Cu_2.

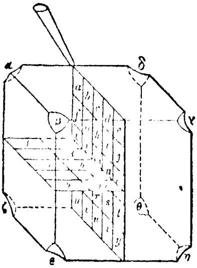


FIG. 20.—Cube showing liquation of Silver and Copper Alloys.

In 1875 the question was taken up by Roberts-Austen, who repeated Levol's experiments. He drew attention to the influence of the rate of cooling on liquation, and showed that in the case of an alloy containing 925 parts of silver and 75 parts of copper very slowly cooled in a cubical mould 45 mm in side, the maximum difference in composition was only 1·1 per thousand, but as much as 13 per thousand when rapidly cooled. His figures are given below, together with a diagram (fig. 20), showing the position in the cube corresponding with the assays:—

Vertical Plane	*a*	925·7
	b	925·0
	c	925·0
	d	925·0
	e	925·4
	f	924·3
	g	925·0
	h	925·3
	i	925·3
	j	925·3
	k	924·3
	l	925·3
	m	925·3
	n	924·4
	o	925·0
	p	924·3
	q	925·0
	r	925·3
	s	925·0
	t	924·9
	u	924·3
	v	924·7
	w	924·9
	x	924·9
	y	925·3

Horizontal Plane	1.	924·8
	2.	925·0
	3.	924·9
	4.	924·9
	5.	925·0
	6.	925·1
	7.	925·1
	8.	925·1
	9.	925·0
	10.	925·0

Corners	α	924·1
	β	924·1
	γ	924·1
	δ	924·4
	ε	924·0
	ζ	924·2
	η	924·2
	θ	923·9

Dip assay, 924·9. Maximum difference (between the centre and the corners) 1·40 per thousand

Some years later Roberts-Austen returned to the subject, and by means of cooling curves taken with the recording pyrometer showed that Levol's alloy was the only one which solidified at a definite temperature. Heycock and Neville, and Osmond have also shown that Levol's alloy is the true eutectic of the series.

Mr E. Matthey has investigated the liquation of alloys of gold and silver containing lead and zinc as obtained in the extraction of gold by the cyanide process, and his results are extremely important. An ingot of this type weighing 120 ozs. was found to contain 662 parts of gold per thousand at the bottom corner and only 439 at the top. Another ingot weighing 400 ozs. and containing 16·4 per cent. of lead and 9·5 per cent. of zinc was found, on separating the whole of the precious metals, to contain gold 514.0 parts per thousand, and silver 75.8 parts per thousand, and its value was reckoned at £1028. The value, however, as calculated from the mean of fourteen assays on the ingot was only £965. In the case of gold and zinc Matthey found that the gold tends to liquate towards the centre of the mass, but only slightly.

An alloy containing 900 parts of gold and 100 of zinc in the form of a sphere 3 in. in diameter was found to be only 1 to 2½ parts per thousand richer in the centre than at the outside. Lead behaves in a similar manner; but the liquation is more marked, the centre of a sphere containing 30 per cent. of lead being 29 parts per thousand richer than the outside. When both lead and zinc are present the liquation is still more marked, and in the case of an alloy containing 15 per cent. of lead and 10 per cent. of zinc the sphere contained 657 parts per thousand at the top, 785 in the centre, and 790 at the bottom. In connection with these alloys it is a curious fact that if the quantity of silver present is not less than two-thirds that of the lead and zinc together, they show very little tendency to liquate, and an alloy containing 55 per cent. gold, 7 per cent. zinc, 18 per cent. lead, and 20 per cent. silver, was found to be practically homogeneous.

CHAPTER III.

METHODS OF INVESTIGATION.

THE experimental difficulties encountered in any attempt to inquire into the nature and constitution of metals and alloys are by no means inconsiderable, and until comparatively recently the subject has been one for speculation and hypothesis rather than for any positive knowledge. These difficulties, however, have been largely overcome by the improved methods of modern research, and before dealing with the constitution of alloys it may be well to consider the various methods which have been employed in their investigation.

These have been conveniently classified by Roberts-Austen and Stansfield under the following heads:—

1. The Chemical Grouping of the Metals in a Solid Alloy.
2. The Separation of the Constituents during Solidification.

The first of these includes the following methods of investigation:—

a. The specific gravity of alloys.
b. The electrical resistance of alloys.
c. Diffusion of metals in alloys.
d. Electrolytic conduction.
e. Thermo-electric power.
f. The heat of combination of metals to form alloys.
g The electromotive force of solution of metals and alloys.
h. Isolation of the constituents of alloys by chemical methods.
i. Microscopical examination of alloys.

The second group deals with those methods involving a study of the separation of the constituents of an alloy on solidification, and includes—

(*a*) Measurement of fall of temperature during solidification by means of a pyrometer.

(*b*) Mechanical separation of the constituents of an alloy by heating to definite temperatures, and draining off or pressing out the liquid portion.

(*c*) Investigation of the changes in the magnetic character of certain alloys during heating and cooling.

The first four of these methods, viz. the determination of specific gravity, electrical resistance, diffusion and electrolytic conduction, have already been considered under the "Properties of Alloys," and need not be dealt with here.

Thermo-electric Power.—This property has been suggested as a means of throwing light on the nature of alloys, but has not been very fruitful in results, owing to the fact that a change in thermo-electric power may be caused by an allotropic as well as a chemical change.

The Heat of Combination of Metals to form Alloys.—A great many metals evolve heat when united, such as aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead; while the union of others, such as lead and tin, is accompanied by an absorption of heat. In this case the absorption of heat is small; but there is an example of an alloy, first described by Mohr, in which a very marked lowering of temperature can be produced. This alloy is formed by taking finely divided tin, lead, and bismuth in their equivalent proportions and rapidly mixing them with eight equivalents of mercury. In this way the temperature of the mixture will actually fall from +17° to −10° C. The determination of the heat of combination may be made by adding one metal to another in the molten state; but in the case of solid alloys the determination can only be arrived at by indirect methods. One such method consists in comparing the heats of solution of the alloy and of the separate metals in acids; but this method is open to objections. Lord Kelvin, Galt, and Gladstone have made determinations of the heat of combination; but, so far, the results have not added much to our knowledge of the constitution of alloys.

Baker (*Phil. Trans.*, vol. cxcvi. p. 529) has made determinations of the heat of combination of a large number of copper alloys. The method adopted consists in determining the difference between the heats of dissolution of the alloy and an equivalent weight of its constituents in a suitable solvent. The solvents employed were an aqueous solution of chlorine, a mixture of ammonium and ferric chlorides, and a mixture of ammonium and cupric chlorides.

In the case of the copper-zinc alloys the experiments show that—

1. There is an evolution of heat in the formation of all the alloys.

2. This evolution of heat reaches a maximum in the case of the alloy corresponding to the formula $CuZn_2$ (*i.e.* 32 per cent. of copper).

The Electromotive Force of Solution of Metals and Alloys.—This method has been used by Laurie, and has given most valuable evidence as to the existence of compounds in alloys. The method, as employed by Laurie, depends upon the fact that if in a galvanic cell—say, for example, a Daniell cell—the zinc plate is replaced by a compound plate made by joining together rods or plates of copper and zinc, the electromotive force is not altered; this is the case even if the zinc surface is only one thousandth part of the copper surface. If now the zinc plate in a Daniell cell is replaced by zinc alloys containing increasingly large percentages of copper, it is found that the electromotive force does not vary appreciably until an alloy containing 33 per cent. of copper is reached, when there is a sudden fall in the electromotive force. From this it is argued that in this alloy there is no free zinc present; but that it is all in combination with the copper, and forms an alloy which may be represented by the formula $CuZn_2$. In the same way with the copper-tin alloys, a sudden change in the electromotive force is noticed when the composition of the alloy corresponds to a formula $SnCu_3$. Moreover, if an alloy containing an excess of tin be employed the excess of tin is dissolved out until the same alloy $SnCu_3$ is reached, when no further change occurs. These results bear out the evidence obtained from the determinations of the density, thermal and electrical conductivity, and also the microscopical examination and cooling curves. These will be discussed later.

Isolation of the Constituents of Alloys by Chemical Means.—It frequently happens that one constituent of an alloy is less soluble in a given solvent than the remainder of the alloy, and this is more especially the case when compounds are present. It is therefore possible, by using a suitable solvent, to dissolve away the more soluble portion, and this can often be facilitated by the employment of an electric current. The residue can then be filtered off and analysed. Photograph 4 is an example of a compound separated in this way.

The Microscopical Examination of Alloys.—The evidence afforded by the microscope, in relation to the constitution of alloys, has been of such value that it may with advantage be considered at some length.

The systematic study of the structure of metals as revealed by the microscope was first undertaken by Dr Sorby of Sheffield as an introduction to the study of meteoric irons. "It was a natural thing," he says, "that I should be led from the study of the microscopical structure of rocks to that of meteorites, and in order to explain the structure of meteoric iron I commenced the study of artificial irons." He began this study in 1863, and in the following year his paper *On a New Method of Illustrating the Structure of various Kinds of Steel by Nature Printing* was published by the Sheffield Literary and Philosophical Society. In 1865 his paper *On the Microscopical Structure of Meteorites and Meteoric Iron* was published by the Royal Society. Nothing further appears to have been done until Prof. Martens published in 1878 the results of his investigations, which were carried out quite independently. The importance of the study of the microstructure of metals and alloys was soon recognised, and the work of Dr Sorby and Prof Martens was taken up and extended by Wedding, Osmond, Andrews, Behrens, Howe, Charpy, Le Chatelier, Roberts-Austen, Stead, and many others.

In order to study the structure of a metal or alloy by means of the microscope it is first necessary to prepare a polished surface, and for this purpose a section of convenient size must be obtained. In the case of comparatively soft alloys this may be effected by sawing through the alloy with a hack saw and then filing into shape. In the case of hard and brittle alloys a diamond cutter may be used, but a simpler method consists in breaking the alloy and selecting a fragment with a comparatively smooth face. This face is then ground down on an emery wheel until flat. The size and shape of the sample to be polished will depend upon circumstances. It may be that a section of thin wire, or of a small turbine blade, is to be polished; or it may be necessary to examine a firebox plate or a large casting. In the case of small sections some skill and ingenuity is required in the polishing, while in the case of larger samples from which a portion has to be cut the selection of the sample must be made with discretion. In any case, the surface to be polished should not be much more than half an inch across, or the labour of polishing will be excessive.

Thin sections can be polished most readily by first embedding them in a larger piece of metal of similar hardness. This can sometimes be effected by electro depositing metal of sufficient thickness upon them and then polishing the whole section, but in the case of simple sections, such as thin sheet, it is usually simpler to make a saw cut in a piece of metal, insert the sheet, and then close the cut by squeezing in a vice or hammering The two can then be filed up as one piece.

In whatever way the sample is taken, great care should be exercised during filing to prevent tearing of the surface After finishing on the smoothest file the section is now rubbed down on emery papers of increasing fineness, using first the ordinary English papers and then those of French make used by steel engravers, and marked 0 to 0000. The grinding on each paper must be continued until the scratches produced by the previous paper have entirely disappeared, when the next paper is substituted and the section turned through an angle of 90°, so that the new scratches are at right angles to the previous ones. In this way it is easy to see when the coarser scratches have disappeared. This preliminary polishing is most rapidly performed by attaching the emery papers to the surfaces of wooden blocks or wheels, which are made to revolve at a high rate of speed. After rubbing down on the last emery paper the surface should be free from all coarse scratches, and is now ready for the final polishing. Various methods have been devised by different workers for the final polishing of the section, and some of these will now be dealt with.

For rough work the section may be polished on a wheel covered with chamois leather or broadcloth, upon which a small quantity of fine dry jeweller's rouge has been sprinkled. For finer work the wheel should be covered with broadcloth which is kept wet, and well washed rouge employed. Wet polishing may take longer, but is far more satisfactory than dry.

Rouge suitable for polishing is prepared in the following way A quantity of jeweller's rouge is stirred up with a large bulk of water (about 50 grams of rouge to a litre of water) in a large jar or beaker, and is then allowed to stand for thirty seconds and the liquid decanted This is allowed to stand for some time, when the water is poured off, and the rouge which has settled is used for the polishing.

With some alloys it is well to avoid the presence of water, and in these cases the rouge may be moistened with a little paraffin This method is very successful in the case of copper and copper alloys

Le Chatelier has made a number of experiments on the subject of polishing, with a view to increasing the speed of the manipulation He points out that in the washing of powders the quantity of carbonate of lime in the water is quite sufficient to cause the formation of lumps, containing both coarse and fine particles, and he recommends the following method The powder is first treated with water containing one part of nitric acid in one thousand of water, in order to dissolve any salts present The mixture is stirred, allowed to settle, and the clear liquid decanted The process of washing and decanting is now continued with distilled water until the acid is removed and the settling takes place more slowly The separation of the powder is then effected by adding two cubic centimetres of ammonia to each litre of water, and the top portion of the liquid is syphoned off at intervals of fifteen minutes, one hour, four hours, twenty four hours, and eight days. After the removal of the twenty four hours powder the finer particles still in suspension may be caused to settle rapidly by adding a small quantity of acetic acid to the liquid.

The powder in the first deposit is unsuitable for polishing, and the second and third are somewhat coarse, but the deposits collected between the first and the eighth day constitute the true polishing powders

The powders so prepared are mixed while still wet with thin shavings of very dry Castile soap, in the proportion of one part of dry soap to ten parts of the wet powder The mixture is melted in a water bath and allowed to cool, stirring continuously, until the mass begins to thicken; it is then poured into tin tubes similar to those in which oil paints are kept

Le Chatelier has found the following substances to be the most satisfactory Alumina obtained from the calcination of ammonia alum, commercial flour emery, oxide of chromium obtained from the calcination of ammonium bichromate, and oxide of iron obtained from the calcination of iron oxalate. Alumina gives far better results than the others.

These are the usual methods for obtaining a polished surface; but when soft metals have to be dealt with, such as lead, it is extremely difficult to obtain a good polish, and only the slightest pressure must be used To overcome this difficulty Ewing and Rosenhain have adopted a method of obtaining a smooth surface without having recourse to any mechanical polishing This method is especially useful in the case of research work carried out on easily fusible metals and alloys, and consists in pouring the molten metal on to a smooth surface such as glass, mica, or polished steel, in contact with which it is allowed to solidify. In practical work, however, it is obviously not permissible to melt the alloy, and the specimen must be polished For this purpose a little Globe metal polish and chamois leather will be found quite as satisfactory as more elaborate methods

When an alloy which is composed of constituents of different degrees of hardness is polished on a soft material, such as leather, cloth, or parchment, the hard constituents will appear in relief, and a preliminary examination of the polished surface is frequently of great value in affording information as to the relative hardness of the constituents of an alloy. As a rule, however, it is necessary to subject the polished surface to the corroding action of some chemical reagent in order to distinguish the constituents. This process is known as "etching." The reagents most frequently used are the various acids, but alkalis, alkaline sulphides, and many other reagents are also used, either in aqueous or alcoholic solutions. Some alloys are most satisfactorily etched by placing the polished specimen in a salt solution and connecting it with the positive pole of a battery, while the negative pole is connected with a piece of platinum foil.

In addition to the ordinary methods of etching there is the method of "heat tinting," which consists in simply heating the specimen in air until the polished surface assumes a decided colour due to slight oxidation, and then cooling quickly by floating on mercury. This method has proved of the greatest value in the hands of Mr Stead, who has shown that it is the only satisfactory method by which carbide and phosphide of iron can be distinguished when associated in iron. It is usually sufficient to heat the specimen on a hot plate, but if any definite temperature is desired a bath of molten tin or lead may be employed. Modifications of this method consist in heating the specimen in gases, such as sulphuretted hydrogen, in order to obtain a film of sulphide or other compound in place of the oxide.

In special cases etching may be effected by means of gases, and the author has found this method of great value in the study of oxides in metals. For this purpose hydrogen is used, the polished specimen being placed in a heated combustion tube through which pure dry hydrogen is passed. The oxides are reduced by the hydrogen, and incidentally the crystalline structure is developed. This, however, is simply due to the heating and not to any action by the hydrogen, as the crystalline structure is equally well developed by any neutral or non-oxidising gas.

The methods of etching are so numerous that it is impossible to deal with them except in a general way, but the more important reagents may be briefly described.

For steel and iron alloys the most useful etching agent is a 5 per cent. alcoholic solution of picric acid. The specimen after polishing is merely dipped in this solution for a few seconds and then washed in alcohol and dried.

For bronzes, brasses, German silver, and nearly all copper alloys a 10 per cent. aqueous solution of ammonium persulphate will be found the most satisfactory. This reagent was suggested by the author many years ago on account of two useful properties which it possesses. Firstly, the etching is effected by simple immersion of the specimen, no rubbing being required as in the case of some other etching agents. This is an important consideration with soft alloys which are very easily scratched by rubbing. Secondly, the action takes place without the formation of gas bubbles, which are always liable to adhere to the polished surface and cause uneven etching. One precaution, however, must be observed in the use of ammonium persulphate—the polished surface must be absolutely free from oil or grease. To ensure this it is advisable to give the sample a preliminary treatment with soda or potash, followed by washing in water before immersion in the persulphate

For antifriction and other white metal alloys a perfect etching agent remains to be discovered, but strong hydrochloric acid will be found as useful as any

Aluminium alloys may be etched either with dilute acid, preferably hydrochloric, or with caustic soda or potash

Silver alloys may be etched with nitric acid or ammonium persulphate as in the case of copper alloys; and gold alloys require the use of aqua regia

The complete microscopical examination of a metal or alloy should be carried out in three stages First, the specimen should be simply polished and examined under both low and high powers. This will afford information as to the relative hardness of the constituents, and will also reveal the presence of blowholes, cracks, and included foreign matter, such as slag, cinder, or unalloyed metal The second examination should be made after slightly etching the polished surface in order to distinguish the constituents This is the most difficult part of the whole process, and great care should be taken not to overdo the etching. The safest method is to etch very lightly and examine, then etch a little further and again examine, and continue the etching until the separate constituents are clearly shown. For the third examination the specimen should be deeply etched with a stronger reagent in order to show up the crystalline structure of the metal. The first and third examinations can usually be carried out with comparatively low magnifications, but the second often requires magnifications of a thousand diameters or more to resolve an alloy into its components.

If it is desired to preserve the specimens for future reference they may either be oiled or the polished surface moistened with a solution of paraffin wax in benzol. This leaves, on drying, a thin film of paraffin which can easily be removed when the specimen is required for re-examination, by wiping with a cloth moistened with benzol. La Chatelier recommends the use of a solution of guncotton in amyl acetate, which leaves a thin film of transparent varnish. This film does not interfere in the least with the examination of the specimen even under the highest powers.

When the specimen has been prepared it requires to be mounted in order to place it on the stage of the microscope, and this mounting requires a little care in order that the surface may be at right angles to the optical axis of the microscope. With a little practice this difficulty can be readily overcome, but one or two mechanical devices for ensuring a perfectly level surface may be briefly described. The simplest of these merely consists of a number of short lengths of brass tube of different diameters which have been carefully cut so that their ends are perfectly true. The specimen to be examined is placed on a glass slip, with the polished surface downwards, and a brass tube is selected which will just pass over the specimen. A quantity of clay or soft wax is then pressed into the tube containing the specimen until it more than fills the tube, and then a glass slip is placed on the top and pressed into contact with the brass ring. Another device has been placed upon the market, and is shown in fig. 21. This consists of two horizontal plates, the upper one being capable of vertical movement, but always remaining parallel to the lower one. The specimen is placed with its polished surface on the lower plate, and the upper plate, carrying a glass slip to which some suitable clay or wax is attached, is lowered into contact. If necessary it can be clamped in position until the mounting medium has set.

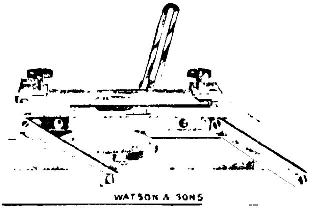


FIG. 21.—Levelling Device for Micro Sections.

To obviate the necessity for mounting the specimen several convenient metal-holders have been devised. Fig. 22 is a simple form of metal holder, consisting of a metal strip with a raised centre in which there is an aperture. The specimen is held with the polished surface against the under side of the aperture by means of elastic bands.

Fig. 23 shows a combined metal-holder and levelling arrangement The specimen is held by two rotating jaws, and can be levelled by means of the screws A, B, and B1.

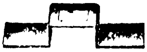


Fig 22 —Simple Metal holder for Specimens

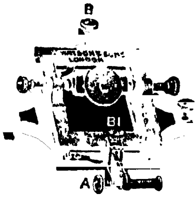


Fig 23. Combined Metal-holder and Levelling Device.

It is obvious that the examination of metals must be conducted by reflected light, and the illumination may be either oblique or vertical. Oblique illumination is only possible with low powers, and for this purpose natural illumination is sometimes sufficient. In most cases, however, a parabolic reflector is desirable, if not necessary A convenient form of reflector is that known as the Sorby-Beck reflector, and shown in fig. 24. It is made to fit on to the objective, and is also supplied with a small vertical reflector which can be instantly placed in position or dispensed with by a turn of the screw.

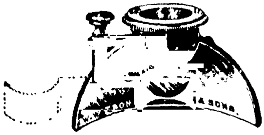


Fig. 24 —Sorby-Beck Illuminator.

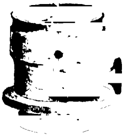


Fig. 25 —Mirror Illuminator.

For high-power work the illuminator must be placed behind the objective, and the reflector in this case may be either a glass prism or a very thin glass disc placed at 45° to the optic axis These two forms of illuminator are shown in figs 25, 26, and 27. It is obvious that in the case of the disc reflector only a portion of the light is utilised, whereas with the prism the whole of the light is reflected This may be a distinct advantage when a powerful source of light is not available. It must be noted, however, that for use with a prism illuminator the objectives must be specially constructed with short mounts so that the glasses may be as close to the prism as possible Both illuminators may be fitted with stops or diaphragms, so that the amount of light admitted may be varied as desired These will be found useful when the section under examination has a brilliantly re-flecting surface, and also when high power oil-immersion objectives are being used.

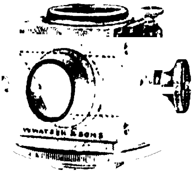


FIG 26. -Mirror

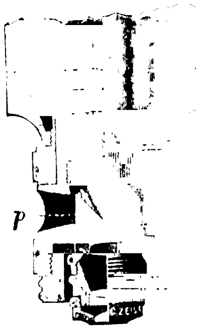


FIG 27. Prism Illuminator

As regards the optical equipment of the microscope, three or four objectives and two eyepieces are all that are required for ordinary work. Two projection eyepieces, described by the makers as No 2 and No. 4, should be chosen, as they are specially adapted for photographic work, and in conjunction with objectives of 16 mm, 8 mm, and 2 mm. focus will give any degree of magnification from about 50 to 2000 diameters. For very low magnification a projection lens of 35 mm. focus, and used without an eyepiece, will be found useful.

The following table gives the magnifications obtained with these objectives calculated for a tube length of 160 mm. and a distance from the eyepiece to the focussing screen of 1 metre:—

Focus in mm.	No 2 Eyepiece.	No 4 Eyepiece.
16	125	250
8	250	500
2	1000	2000
35	28	(without eyepiece)

Any form of microscope may be used if it is only desired to examine specimens, but if photographic records are to be obtained it is advisable to employ one of the special microscopes which have been designed for the purpose. These are fitted with exceptionally wide body tubes in order to minimise the reflections from the inside of the tube.

The microscope and camera may be used either in a vertical or horizontal position when moderate magnifications are required, but when high-power objectives and a long camera extension are employed the horizontal position becomes a necessity An apparatus, therefore, which is intended for any degree of magnification should be placed in this position

As regards the illumination, an electric arc lamp with automatic feed is perhaps the most satisfactory; but any brilliant light, such as an incandescent gas lamp, an oxyhydrogen light, acetylene or Nernst lamp, will give good results. In any case a condenser should be placed between the light and the reflector to concentrate the rays as much as possible.

For photographic work Le Chatelier recommends a monochromatic light on account of the chromatic aberration of the objectives, which are never completely free from this defect. He obtains a suitable light by passing the rays from a mercury arc lamp in vacuo through a solution of sulphate of quinine, which only allows the indigo, green, and yellow rays to pass, and as the green and yellow rays have little or no action upon an ordinary plate the light may be considered monochromatic.

For all ordinary work, however, these refinements are unnecessary, and a simple arc light and colour screen will give perfectly satisfactory results. Fig. 28 shows a small and convenient arc lamp by Zeiss The positive carbon is placed in a horizontal position and the whole of the light from the crater is available without interference by the negative carbon. The lamp takes only 5 amperes, so that it can be used on the ordinary lighting circuit, and, in conjunction with the aplanatic condenser supplied by the makers, gives a light equal to an ordinary 20 ampere lamp

Fig. 29 shows a form of microscope specially made for photographic work, by Zeiss of Jena. It is used in conjunction with a camera in a horizontal position, and focussing is effected by a rod (St) connected by a universal joint (Tr) with a small milled head which, in its turn, engages the large milled head M

The photographs illustrating this book were taken with a microscope of this form which the author has had in constant use

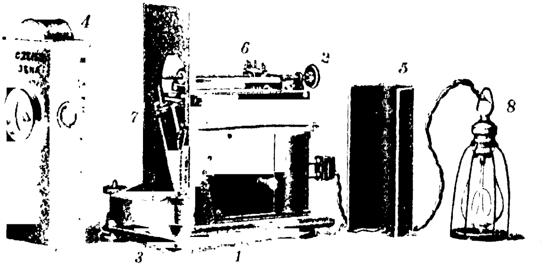
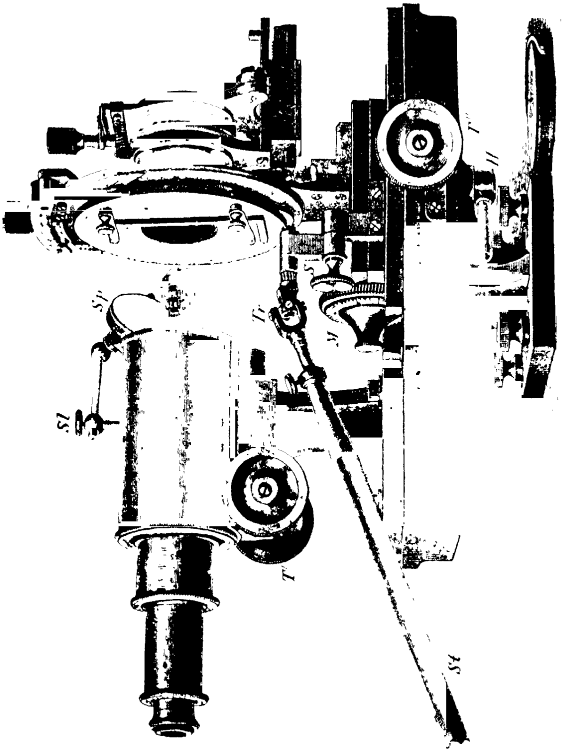


Fig. 28 —Small Zeiss Arc Lamp for Photomicrography

and with perfect satisfaction for the last nine years Fig. 30 illustrates a similar form of microscope intended for use with a simple form of camera in a vertical position

A complete photomicrographic outfit capable of meeting all requirements is made by Zeiss and shown in fig 31. In this instrument the camera and optical parts are arranged on separate tables so that the vibration caused by pulling out the shutter of the dark slide is not communicated to the microscope The optical outfit consists of the small arc lamp already described, and an optical bench carrying the condensing lens system and any absorption cells or light filters which may be required. The microscope stands on a sole plate provided with levelling screws, and can be used either in the horizontal or vertical position. The camera, which is made in two sections, is mounted on three steel bars sliding on rollers, so that it can be readily moved from the microscope to allow of visual observation Each section of the camera is made to slide on the steel bars and can be clamped in any position. In this way any camera extension can be used from 5 ins. to 5 ft. The final focussing is



effected on the screen by means of a rod and Hook's key arrangement.

Fig. 32 illustrates a form of microscope by Reichert in which the stage is placed in a horizontal position so that mounting of

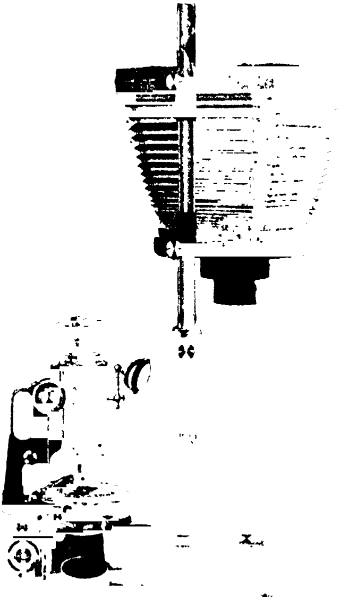


FIG. 30 —Vertical Microscope and Camera.

the sample under observation is unnecessary. Two tubes are provided, one for observation and another at right angles for photography. The optical arrangements are shown in fig. 33. A beam of light from any suitable source is reflected from the prism P_1 through the objective on to the specimen and back

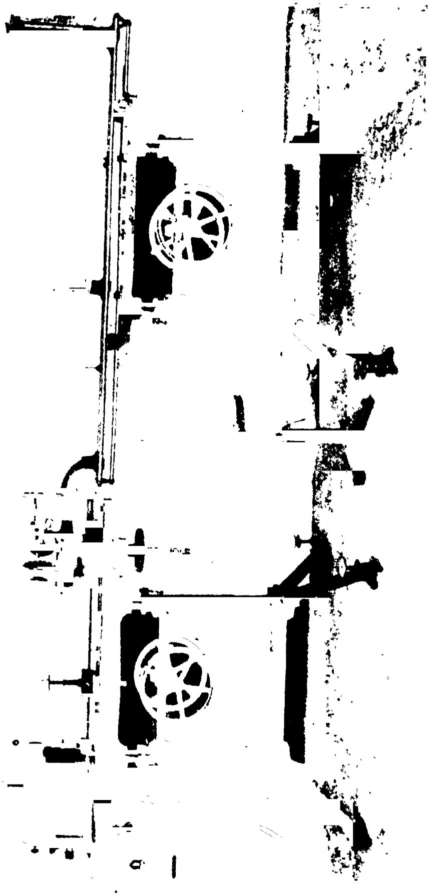


Fig. 31 —Zeiss Outfit for Photomicrography.

through the prism P_2. After focussing, the prism P_2 is rotated through an angle of 90° about an axis at right angles to the plane

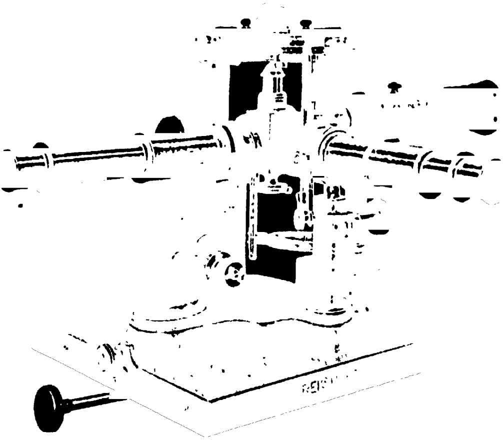


FIG. 32. Reichert Metallographic Microscope

of the stage, which throws the beam of light through the second tube to which the camera is attached. Fig. 34 shows the complete outfit for photomicrography.

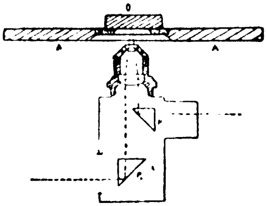


FIG. 33. - Optical arrangement of Reichert Microscope

Success in photographic manipulation can only be acquired by practice and experience, but a few hints may be useful to those who are beginning the study of alloys by means of the microscope.

In the first place, the use of a light filter placed between the source of light and the microscope will give better results, and if the source of light is an arc lamp, a piece of green glass of the kind commonly known as "signal" green will be found perfectly satisfactory. Any well-known brand of photographic plates may be used, the speed of the plates selected depending to a great extent on the source of illumination. If a weak light is being used, then rapid plates may be used to shorten exposures; but if an arc light is employed, the plates described by the makers as "Ordinary" will probably be the most useful. An exposure of approximately 5 seconds is the most convenient, if longer there is risk of movement, and if shorter than 3 seconds it is difficult to time them accurately without a shutter, and the use of a shutter involves serious risk of vibration unless very carefully arranged.

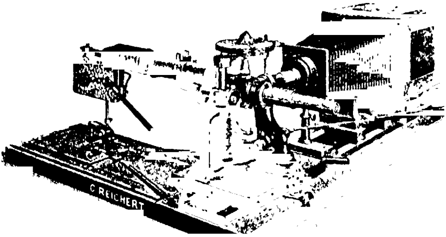


Fig. 34.—Reichert Microscope and Camera.

Slow plates are sometimes recommended as possessing finer grain than rapid plates. There was some reason for this in the early days of the photographic dry plate, but the grain of the fastest modern plate, even when using the highest powers of the microscope, is negligible. A commoner mistake, and one frequently found in text-books, is the statement that slow plates are preferable as they give greater "contrast." The worst fault which every beginner in photography has to overcome is this temptation to produce negatives with great contrasts, and a large majority of published photomicrographs suffer from the same defect. Harsh contrasts are seldom seen under the microscope, and are usually confined to cracks, blowholes, and certain slag inclusions. When they occur in a photograph it is usually the result of bad photography or bad etching.

In order to obtain the best results, backed plates should be employed, as halation, or reflection from the back of the plate, is a common source of trouble in photomicrographic work

When photographs are taken it is important that standard magnifications should be adopted The great value of photomicrographs as a record lies in the readiness with which they can be compared, and this is rendered extremely difficult if all degrees of magnification are used It was pointed out in the preface to the first edition of this book that experience had shown that magnifications of 100 and 1000 diameters fulfilled all that was necessary in the great majority of cases, and these standards have been adopted by a large number of metallographists

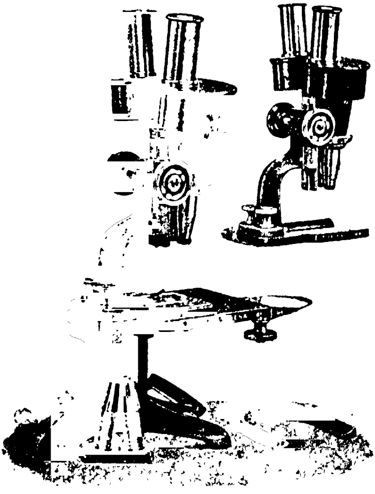


FIG. 35 Stereoscopic Microscope

Before leaving the subject of microscopes, two instruments may be briefly described which have proved of service in the study of metals and alloys.

Fig. 35 is a stereoscopic microscope which has proved useful in the examination of uneven surfaces such as fractures

Fig. 36 is a micrometer microscope of recent introduction which is likely to prove of great service to the metallurgist. It is capable of measuring distances up to 20 mm. with an accuracy of 0·01 mm., and a useful feature of the instrument is that by loosening the screw K the stem of the microscope can be slipped out of the split sleeve H, thus separating the stand from the upper body, which can then be secured by its stem to any laboratory stand and used in any position desired. Another model of this microscope is designed for the measurement of two distances at right angles to each other.

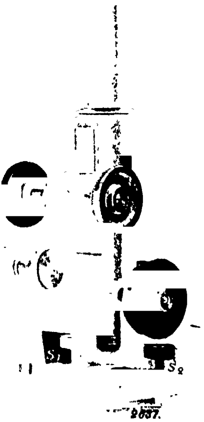


FIG. 36.—Measuring Microscope.

Measurement of Fall of Temperature during Solidification.—In 1884 Dr Guthrie published the results of an investigation dealing with changes which take place during the solidification of alloys, and he comes to the conclusion that there is a close analogy between the solidification of molten granite and a fluid alloy. Just as, in the case of a mass of molten granite, the quartz and felspar crystallise out leaving the mica still fluid, so in the case of an alloy certain constituents solidify until "the alloy of minimum temperature of fusion" is left behind. This most fusible alloy of the series Guthrie calls the *eutectic* alloy, and he points out that the constituents of this alloy are not in simple atomic proportions. "The constitution of eutectic alloys," he says, "is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties less definite."

Guthrie was only able to deal with alloys of low melting-point, and, owing to the experimental difficulties involved in the accurate measurement of high temperatures, this method of investigation was practically neglected until the introduction of the Le Chatelier pyrometer. The study of pyrometry belongs rather to the domain of physics than metallurgy; but the use of pyrometers in the study of alloys has become so important that a brief description of the more useful types may not be out of place.

Pyrometers suitable for the study of alloys, where the temperatures of small masses of metal have to be accurately determined, may be divided into two classes: 1, resistance pyrometers; and 2, thermo-electric pyrometers.

The measurement of temperature by means of the resistance pyrometer depends upon the increase in resistance of a platinum wire when heated. In the Callendar & Griffith's resistance pyrometer a fine platinum wire is wound on a mica frame, which is enclosed in an outer protecting case. The ends of the platinum wire are connected by copper leads either to a direct reading instrument or to a clockwork recorder. In order to avoid the introduction of any error due to the variation of the temperature of the wires connecting the thermometer with the recorder, two similar leads, not connected with the coil, are passed down the whole length of the thermometer. This thermometer may either be connected with a direct reading indicator or an automatic recorder.

The measurement of high temperatures by means of a thermo-electric couple was suggested by Becquerel in 1826; but a satisfactory couple was not obtained until 1887, when Le Chatelier published his researches on the platinum—platinum-rhodium couple. In this apparatus the couple is formed by joining or fusing together the ends of two wires, one of absolutely pure platinum and the other of pure platinum alloyed with 10 per cent. of rhodium. When one junction of these wires is heated an electric current is generated, and this current has been proved, by comparison with the air thermometer of the Royal Physical Institute, to be proportionate to the heat applied. The wires are 0·6 millimetres in diameter, and the current generated is approximately ·001 volt for every hundred degrees Centigrade.

In order to protect the wires from injury they are enclosed in porcelain or fireclay tubes. The Royal Porcelain Factory in Berlin manufacture tubes which will resist a temperature of 1600° C., but a simple fireclay tube is often quite satisfactory. The couple is inserted in the tube with a thin strip of mica between

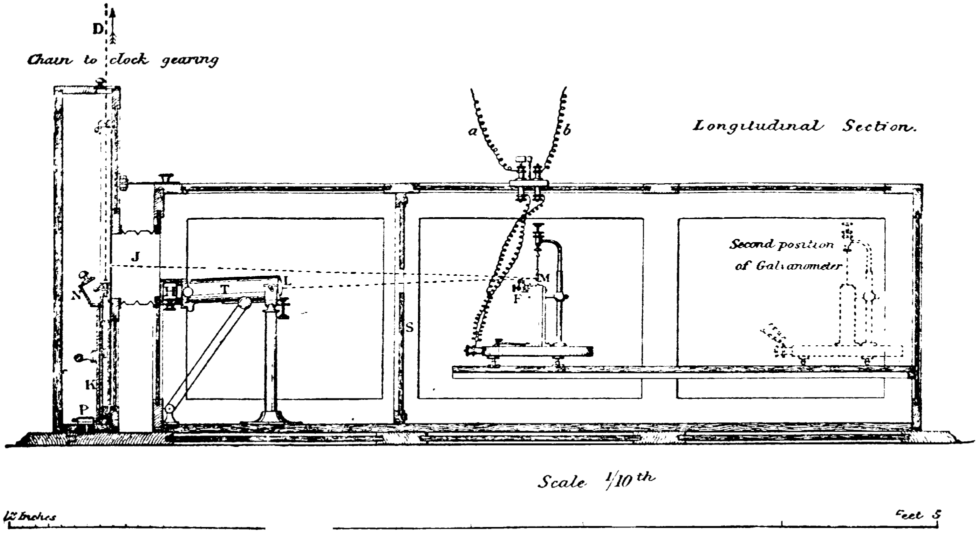


FIG. 37.—Roberts-Austen's Autographic Recording Pyrometer.

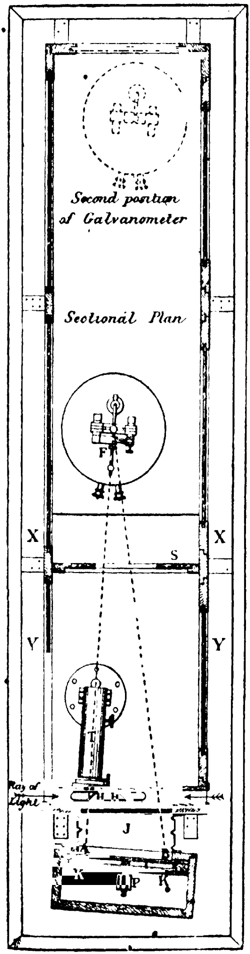


FIG. 38.—Sectional Plan of Roberts-Austen's Autographic Recording Pyrometer.

the wires in order to prevent a short circuit. The other end of the wires forming the couple should be maintained at a constant temperature, if accurate measurements are to be taken; and to ensure this they are enclosed in glass tubes, which are immersed in ice or else in water whose temperature is accurately known. The thermo-couple measures the difference in temperature between the heated junction and the "cold junction." The copper leads are connected with a galvanometer of the d'Arsonval type, which may be arranged for direct readings or used in conjunction with an automatic recorder In the automatic recorder devised by Sir William C. Roberts-Austen mirror galvanometer is used and a beam of light is reflected from the mirror on to a narrow horizontal slit, behind which a photographic plate is caused to move vertically either by clockwork or by means of a water float. The arrangement of the apparatus will be readily understood by reference to fig. 37, which represents the pyrometer used with such admirable results by Roberts-Austen at the Royal Mint.

The camera is about five feet in length and is supplied with three doors, so that the galvanometer is accessible for any necessary adjustments. Connected to the camera by a flexible leather bellows is the apparatus which contains the moving photographic plate. F is the galvanometer, which can be placed in one of two positions, according to the range of temperature to be observed. Inside the camera and immediately in front of the photographic plate is the focussing tube T, containing a lens L which receives the light from the mirror H and throws it on to the galvanometer mirror. Any deflection of the galvanometer mirror causes the spot of light to travel along the slit, and thus traces out a curve on the moving photographic plate.

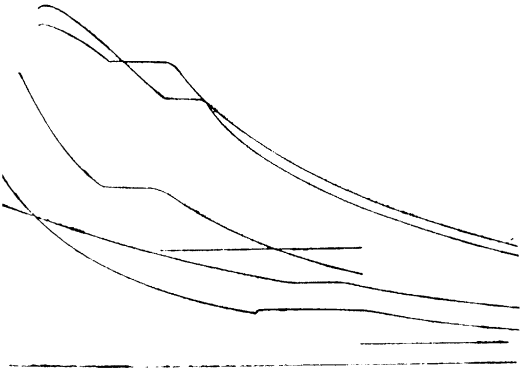


FIG. 39.—Example of Calibration of Pyrometer.

Now it is evident that if the rate of cooling were constant the curve would be the simple resultant of two movements at right angles, and would therefore be a straight line. But the rate of cooling always becomes slower as the body becomes colder, and the actual curve given by a cooling mass is a smooth curve of the form shown in the lower parts of the curves in fig. 39.

If, now, the thermo-couple, suitably protected, is dipped into a mass of pure molten metal—copper, for example—which is then allowed to cool slowly, a different curve is obtained. The temperature falls steadily until the metal begins to solidify, but at this point the temperature remains constant, owing to the latent heat of fusion of the metal, until the whole of the mass is solid. After this "arrest" in the cooling the temperature falls again in the usual way. The resulting curve, then, is similar to those shown in fig. 39 (which represents the cooling curves of the metals tin, lead, aluminium, silver, and copper, together with two straight lines representing the boiling-points of water and sulphur respectively), and this is a typical cooling curve of a pure metal. There are two possible modifications, however, in the case of pure metals which should be noticed. The first of these is observed when the metal is cooled slowly without being disturbed. Under these conditions the temperature sometimes falls two or three degrees below the true freezing-point of the metal before solidification begins. The freezing of the mass is then accompanied by a sudden rise in temperature to the true freezing-point of the metal. This phenomenon is known as *surfusion*, and it will be remembered that it also occurs in the freezing of water and other liquids. An example of surfusion is seen in the cooling curve of tin in fig. 39.

The second modification of the typical cooling curve is not frequently met with, but occurs when a molecular rearrangement takes place in the metal at some temperature below its freezing-point. In other words, the metal at a certain temperature passes from one allotropic modification to another. A molecular change such as this occurs in the case of iron, and is accompanied by an evolution of heat, which is shown in the cooling curve. A further indication of molecular change is shown by the fact that the iron becomes magnetic below this temperature, while before it was non-magnetic. Similar results are obtained in the case of nickel. The magnetic properties of the iron and nickel alloys will be dealt with later.

A number of melting-points of metals have been accurately determined by means of the air thermometer, and these, together with other well-known temperatures, are employed in the calibration of pyrometers. The most useful temperatures for calibration purposes are the following:—

Boiling-point of water	100°
Melting-point of tin	232°
Melting-point of lead	326°
Boiling-point of sulphur	448°
Melting-point of aluminium	657°
Melting point of silver	961°
Melting-point of copper	1084°

It is absolutely necessary that pure metals be used, and in the case of the boiling-points of water and sulphur the thermo-couple must be placed in the vapour of the boiling liquid and not in the liquid itself. Fig. 39 shows an actual calibration of a Roberts-Austen recording pyrometer. In the first place a "datum" line is taken by letting the photographic plate run while the galvanometer is at rest with no current passing. The plate is then run a second time with the thermo-couple immersed in melted tin contained in a small crucible, and so on, all the curves being taken on one plate. The distances between the datum line and the various points are then measured on the plate, and, if a curve is plotted on squared paper with these distances as abscissæ and temperatures as ordinates, an approximately straight line is obtained from which any other measurement of temperature can be easily read off.

It is advisable that a fresh calibration be made from time to time to ensure that both galvanometer and thermo-couple are in proper working order.

In cases where considerable ranges of temperature have to be measured, a pyrometer, such as that just described, is open to the objection that the large angular deflection of the galvanometer mirror is liable to strain the suspending wires and thus introduce a serious error. To obviate this difficulty the current from the thermo-junction is not allowed to pass directly through the galvanometer, but is opposed by a current from a standard Clark cell, which can be regulated and measured by means of a potentiometer introduced in the circuit. In this way only a portion of the thermo-electric current passes through the galvanometer, and the mirror is only deflected through a small angle. An apparatus of this description, however, requires a special arrangement, as the movement of the spot of light has to be watched and the electrical balancing of the current carried out during the operation. In this case the galvanometer is not enclosed in a camera, but the room in which the operation is carried out is somewhat darkened, so that the spot of light can be seen travelling along the horizontal slit without fear of fogging the photographic plate.

Sir William C. Roberts-Austen, in his classical researches at the Royal Mint, employed a water clock consisting of a float carrying a photographic plate which moved upwards between guides. The whole was enclosed in a case provided with a horizontal slit, through which the ray of light from the galvanometer mirror might pass In this apparatus Roberts-Austen introduced a further improvement, by means of which very small variations in the temperature of a cooling body could be detected and measured. This method, which has proved to be of the utmost service in metallurgical research, is known as the "differential" method, and the arrangement of the apparatus is shown in the diagram fig. 40.

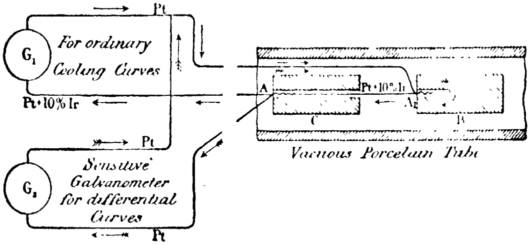

Pt
G₁
For ordinary Cooling Curves
Pt+10% Ir
Pt
G₂
Sensitive Galvanometer for differential Curves
Pt
A
Pt+10% Ir
A₁
C
B
Vacuous Porcelain Tube

FIG. 40.—Apparatus for Differential Curves

B is the mass of metal under examination, and A_1 the thermo-couple connected in the ordinary way with the galvanometer G_1 At A, however, a second thermo-junction is formed which is surrounded by a mass of platinum, C, and connected with a second galvanometer, G_2, as shown in the diagram. In this way the first galvanometer measures the actual temperatures, whereas the second only receives such current as may result from the opposing couples A and A_1—that is to say, it measures the difference in temperature between the masses of metal C and B.

By using three thermo-couples instead of two the connections can be simplified, as shown in fig. 41 (see p. 180 of Roberts-Austen's *Introduction*), and this is the arrangement generally adopted in taking differential curves.

If it is desired to make the irregularities of an ordinary cooling curve appear very pronounced, the curve may be plotted by the inverse rate method as first employed by Osmond in 1886. In this method the intervals of time taken by the sample to cool through equal decrements of temperature are noted and plotted in terms of the temperature.

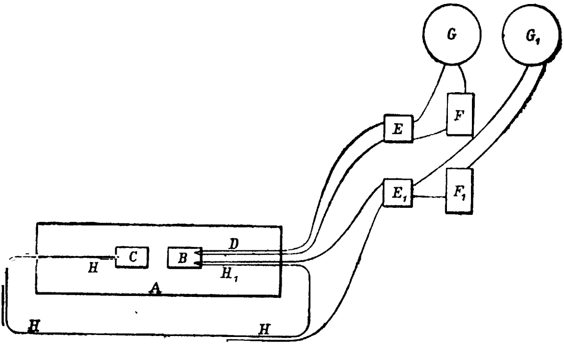


FIG. 41.

A. Electric Furnace
B. Steel under examination.
C. Neutral Metal; Ni-Steel or Platinum
D. Thermo-couple for Temperature

E E_1 Cold-Junctions
F F_1. Resistance Boxes
G. Galvanometer for Temperature.
H H_1. Compound Thermo-couple
G_1. Differential Galvanometer

For works purposes many other forms of pyrometer are largely employed, such as optical pyrometers, radiation pyrometers, etc. These instruments are fully described in the *Introduction to the Study of Metallurgy* in this series, and it is therefore unnecessary to do more than merely mention them here.

Mechanical Separation of the Constituents of an Alloy by Heating to Definite Temperatures and Pressing out the Liquid Portion.—Experiments in this direction are difficult to carry out, but the results are instructive, and serve to confirm the conclusions arrived at by the study of the cooling curves. In 1884

Guthrie described the method and gave some results which he had obtained in the case of alloys with low melting-points. Very little appears to have been done since, but within recent years Roberts-Austen made use of the method in his investigations on the properties of the brasses. The alloy is placed in a steel cylinder provided with two loose plungers, upon which a pressure of about half a ton per square inch is maintained by means of a hydraulic press. The cylinder is gradually heated and the temperature determined by means of a thermo-couple inserted in a small hole drilled in the cylinder. As the temperature rises, a portion of the alloy liquefies and is squeezed out between the plungers; by analysing the extruded portion and noting the temperature at which it became liquid, a very clear idea may be gained of the order in which the constituents of the alloy have solidified and of their approximate compositions

Change in the Magnetic Character of Alloys during Heating and Cooling.--This method of research is limited to a few alloys, but has been of great service in the case of steels and iron alloys. Iron, nickel, and cobalt are the only metals which possess the property of magnetism at the ordinary temperature, and it is well known that these metals, when heated, lose their magnetism at certain definite temperatures. On cooling they again become magnetic, but usually at a temperature somewhat below that at which they ceased to be magnetic; owing to a resistance to change in the metal, to which the name *hysteresis* has been given. The temperatures at which these metals lose and regain their magnetism are known as the points of transformation, and it is generally supposed that the loss of magnetism is due to an allotropic change in the metal. It is of considerable interest, therefore, to determine the magnetic properties of the alloys of these metals and the influence of other metals on the points of transformation. Some metals raise the point of magnetic transformation; others lower it. Nickel, for example, although itself magnetic, lowers the point of transformation of iron; and an alloy containing 25 per cent. of nickel requires to be cooled to - 50° in order to attain its maximum degree of magnetism.

The magnetic properties of the iron alloys have been studied by Le Chatelier, Osmond, and Mme. Curie, whose original papers should be consulted for further details.

Until recently manganese has been regarded as a non-magnetic metal, but it would seem that it is capable of assuming a magnetic condition when alloyed with other metals. Attention was first called to the fact by Hogg at the meeting of the British Association at Edinburgh in 1892, and his observations have since been confirmed by Heusler and others. The principal magnetic alloys of manganese are those with aluminium, antimony, tin, bismuth, arsenic, and boron.

CHAPTER IV.

THE CONSTITUTION OF ALLOYS.

The nature and constitution of metals and alloys naturally attracted the attention of the early metallurgists, and Roberts-Austen has pointed out that Achard, Musschenbroek, and Réaumur were all engaged in the study of alloys in the eighteenth century, but it would appear that Boyle was the first to suggest the line of thought which has led to our present views of the constitution of metals and alloys. Discussing the states of matter, he says: "Even such as are solid may respectively have their little atmospheres"; and he adds: "For no man, I think, has yet tried whether glass, and even gold, may not in length of time lose their weight."

Boyle was therefore clearly of the opinion that the solid state of matter was not far removed from, and was in fact usually accompanied by, the liquid or gaseous states, and two hundred years later his belief was proved to be correct by the experiments of Merget and Demarcay.

In 1860 the same suggestion is made by Matthiessen, who, after describing his experiments on the electrical conductivity of alloys, says: "The question now arises, What are alloys? Are they chemical combinations, or a solution of one metal in another, or mechanical mixtures? And to what is the rapid decrement in the conducting power in many cases due? To the first of these questions," he adds, "I think we may answer that most alloys are merely a solution of one metal in the other; that only in a few cases may we assume chemical combinations." Three years later Graham declared his belief that the solid, liquid, and gaseous states probably always co-exist in every solid substance, and he says: "Liquefaction or solidification may not, therefore, involve the suppression of either the atomic or the molecular movement, but only the restriction of its range." In 1866 he justified this belief by proving that gases were capable of penetrating solid metals. In 1882 Spring produced alloys by compression of the constituent metals, and four years later he declares that "we are led to think that between two molecules of two solid bodies there is a perpetual to-and-fro motion of the atoms." "If," he says, "the two molecules are of the same kind, chemical equilibrium will not be disturbed but if they are different this movement will be revealed by the formation of new substances."

From this time the researches on alloys become more numerous and the development of ideas proceeds more rapidly. In 1889 Heycock and Neville demonstrated the important fact that Raoult's law of the depression of the freezing-point of solvents is in many cases applicable to metals. Roberts-Austen, continuing Graham's work on diffusion, published in 1896 his classical researches on the diffusion of metals, followed by another paper, in which he showed that diffusion took place between metals in the solid state in the same way as in the liquid state, though more slowly. Four years later he was able to prove that gold was capable of diffusing into lead at the ordinary temperature of the atmosphere.

From the foregoing brief historical sketch of the researches into the constitution of alloys it will be seen that the trend of modern research has been to prove that the solid state of matter is closely related to the liquid and gaseous states, and that metals are subject to the same laws which govern the behaviour of liquids and gases. Moreover, just as in the case of inorganic bodies we recognise the existence of elements, compounds, and solutions, so in the case of metals we have pure metals, compounds, and solutions, and it is important to know how these possible constituents may occur in an alloy.

The methods employed in the investigation of the constitution of alloys have already been described, and it only remains to consider the results obtained by their use and the conclusions to be drawn from them. It has already been mentioned that the pyrometer and the microscope have been of the greatest service in determining the constitution of alloys, and we will therefore consider the different types of curve likely to be met with and the conclusions which may be drawn with the confirmatory evidence of the microscope.

If a temperature record, or a "cooling curve," is taken of a pure metal cooling from a temperature just below its melting-point, the curve obtained is a smooth one without any sign of irregularities, but if a similar curve is taken of the same metal cooling from a temperature *above* its melting-point the result is a curve similar to those shown in fig. 39. At first the cooling proceeds normally and a smooth curve is produced, but as soon as the freezing-point of the metal is reached and it begins to solidify, the temperature remains constant and is represented by a straight line until the latent heat of fusion is given out, when the cooling again continues and the remainder of the curve is normal as before. There is only one irregularity in the curve, and the metal freezes or solidifies as a whole at one definite temperature.[1] In some cases, if the metal is very pure and the cooling takes place slowly and without disturbance, the temperature may descend below the true freezing-point of the metal without solidification taking place. When solidification does occur the temperature rises suddenly to the true freezing-point and remains there until solidification is complete. This super-cooling or surfusion of the metal causes a slight depression in the curve at the beginning of the straight line representing the freezing-point, and is shown in the cooling curve of tin in fig. 39.

A simple curve with only one horizontal break, showing that the metal has solidified as a whole at a definite temperature, is characteristic of pure metals, pure eutectics, and homogeneous solid solutions. Chemical analysis accompanied by a microscopical examination will at once indicate which of the three is under consideration.

A word of explanation is, perhaps, necessary as to the meaning of the expression *solid solution*, as it is frequently applied incorrectly. Consider, first, the case of a liquid solution and the characteristics which define a solution When a solid substance is dissolved in a liquid the particles of the solid are so intimately mixed with the liquid that they cannot be seen, even with the aid of the microscope, and the solution is clear. If any particles are visible they are capable of being separated by mechanical means, such as filtration, and they are not in solution. The characteristics of a solution, then, are that the particles of the dissolved substance cannot be detected and cannot be separated by mechanical means. Now the same definition may be applied to solid bodies. In a mass of gold, for example, containing silver, the silver cannot be detected under the highest powers of the microscope, nor is it capable of being separated by mechanical means. The alloy solidifies and crystallises as though it were a pure metal, and the mixture of the two metals is so intimate that there is a strong analogy between it and a liquid solution Van't Hoff therefore described such a mixture as a solid solution, and the expression is now in general use.

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[1] In this case we assume that no allotropic change takes place. See p. 85.

Solid solutions, however, may not always be homogeneous; they may vary in concentration. Thus copper containing a small quantity of tin (not exceeding 8 per cent.) does not separate into two constituents; but it does not solidify at one temperature. As the mass cools down, almost pure copper separates out at first, so that, as solidification proceeds, the portion remaining liquid becomes more concentrated in tin. The only indication of this is found on etching a polished surface, when the unequal action of the etching agent shows itself in shaded bands as seen in photographs 9 and 10.

Most metals are more or less soluble in one another, but the degrees of solubility are very variable. As regards the structure of metals and solid solutions, it may be remarked that they do not crystallise like ordinary liquid solutions, but more closely resemble viscous solutions. Well-defined or idiomorphic crystals are seldom found, while crystallites or the incipient forms of crystals are predominant. On annealing, however, this crystallitic structure is replaced by a well-defined crystalline structure. Photographs 27 and 31 are examples of the crystallitic, and 12, 30, and 34 of the crystalline structure. A curious point to be noted in the crystalline structure is that rolling or hammering produces abundant twinning of the crystals, while in unworked samples cases of twinning are not seen.

The third case of a cooling curve with a single break, viz. that of a pure eutectic, is seldom met with, but will be considered immediately. If, now, a cooling curve is taken of a molten metal to which another metal has been added, the curve may be of three kinds: (1) It may show a single break at a temperature below that of the pure metal, showing that the alloy is a solid solution or a pure eutectic. (2) It may show two breaks, both lower than that of the pure metal, showing that the alloy contains two constituents melting at different temperatures. In most cases, one of the constituents will be found to be a eutectic; but they may both be solid solutions or one of them may be a compound. (3) If the curve shows two breaks, one higher than the melting-point of the pure metal, it may be taken for granted that this break is due to the solidification of a definite compound. The types of curves will be more fully dealt with later, but in the meantime we must define the expressions *eutectic* and *compound*, and consider their microscopical appearance.

The term "eutectic" was first used by Guthrie to indicate the mixture or alloy possessing the lowest freezing-point of a series. This freezing-point is always below that of the mean of the metals of which it is composed. The eutectic structure is composed of the different constituents in juxtaposition, but the structure is always very small and requires a high magnification for its resolution. The constituents of a eutectic may occur in curved plates or laminæ, or in globules, and either or both may be simple metals, solid solutions, or compounds. Types of eutectic structures are shown in photographs 6, 7, 8, and 18. They are very characteristic, and cannot easily be mistaken.

The term *compound* or *metallic compound* is applied to those constituents of certain alloys which resemble chemical compounds in their properties. The formation of these compounds is accompanied by an evolution of heat, and they are almost invariably hard and brittle, with melting-points higher than the mean of their constituents. The metals of which they are composed combine, as nearly as can be judged, in atomic proportions; but their composition cannot easily be determined, as they are occasionally soluble in, or themselves dissolve, the metals of which they are composed. They can usually be separated from an alloy by dissolving away the surrounding metal, either with or without the aid of an electric current, but it is impossible to say whether the compound thus separated is pure or not. Metallic compounds can usually be detected under the microscope unless they happen to be soluble in one of the other constituents, as is sometimes, but not frequently, the case. Occasionally they crystallise out in well-formed crystals exhibiting angles and faces, but more often they simply occur as crystallites. However, the grouping of the crystallites often throws some light on the crystal form. Photograph 2, for example, indicates a very definite arrangement of crystallites, and the compound shown in photograph 4, which has been separated from the alloy by solution, shows a well-formed angle at the extremity of one of the arms. Photograph 5 shows a well-formed crystal of the same compound occurring in the alloy. This is an exceptionally interesting case, as it is not usual to find two metals forming such well-defined compounds. Compounds of metals with the non-metals, however, such as phosphorus, form very well-defined compounds.

Having now considered the possible constituents in an alloy and the types of cooling curve which they produce, the next step is to follow the complete series of alloys formed between any two metals. In order to do this a large number of cooling curves must be taken of alloys varying in composition and their structure examined microscopically. The freezing-points or breaks in the curves are next plotted in the form of a new curve with compositions and temperatures as co-ordinates, so that the freezing-point of any alloy can be seen at a glance. This curve has been described by Gautier, and is now generally known as the "complete freezing-point curve" for that series of alloys.

Le Chatelier has classified binary alloys having normal curves of fusibility under three heads:—

1. Curves consisting of two branches starting from the melting-points of the pure metals and meeting at a point corresponding to the eutectic alloy. A curve of this description is obtained when the two metals are not isomorphous and do not form definite compounds.

The alloys of lead and tin, lead and antimony, and tin and bismuth, belong to this group.

2. Curves consisting of three branches, two starting from the melting-points of the pure metals and a third having a maximum point due to the formation of a definite chemical compound, and crossing the other two in two points corresponding to two eutectics. Examples of this group are found in the alloys of copper and antimony and nickel and tin.

3. A single curve uniting the melting-points of the two pure metals. This is a case of pure isomorphism, which is comparatively rare amongst metals. It is, however, shown in the case of the gold-silver alloys.

The microscopical examination of typical cases of these three curves will illustrate their meaning. As an example of the first curve we will take the alloys of lead and antimony. The freezing-point curve of this series shows a minimum at a point corresponding to 13 per cent. of antimony. If the alloys containing less than 13 per cent. of antimony are examined under the microscope they are found to consist of soft fern-leaf-shaped dendrites of lead surrounded by the eutectic of lead and antimony, the amount of the eutectic increasing as the percentage of antimony increases until the alloy containing 13 per cent. of antimony is reached, when the whole mass is composed of the eutectic. When more than 13 per cent. of antimony is present hard crystals of antimony make their appearance in the eutectic, and these increase as the percentage of antimony increases. Owing to the superior hardness of the antimony crystals they are easily visible by simply polishing and without any etching.

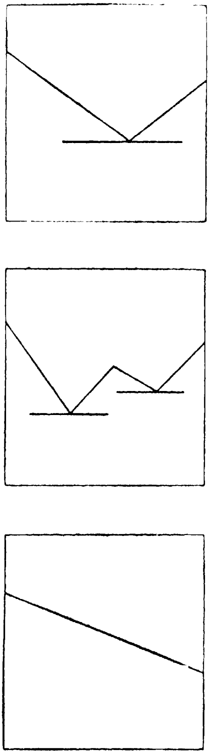

FIG. 42.—Three Curves representing the Constitution of Binary Alloys.

The second type of curve is well represented by the alloys of copper and antimony. In this series there are two eutectics corresponding to the alloys containing 25 and 71 per cent. of copper, while between these two points the curve rises to a maximum corresponding to 60 per cent. of copper. This is the composition of the definite compound $SbCu_2$. Starting with pure antimony, and adding copper in increasing quantities from 0 to 25 per cent., a microscopical examination will reveal crystals of antimony surrounded by a eutectic, the crystals decreasing and the eutectic increasing in quantity until 25 per cent. of copper is reached, when the whole alloy is made up of the eutectic. When more than 25 per cent. of copper is added a new constituent makes its appearance in the form of crystallites having a distinct violet colour. These crystallites increase in quantity until the alloy containing 60 per cent. of copper is reached, which consists entirely of the violet alloy. Between 60 and 70 per cent. the alloys are found to consist of violet grains surrounded by a network of eutectic, and when 70 per cent. is passed dendrites of copper are seen surrounded by the second eutectic.

It will be seen that the alloys which fall under the second group in Le Chatelier's classification, viz. those forming definite chemical compounds, really give the same curves as the alloys of the first group, but duplicated. That is to say, the curve may be divided at the point representing the compound and considering the compound as a separate constituent (which it is), and not as an alloy. The curve is then resolved into two curves of the first group, and represents two freezing-point curves of two series of alloys each formed by a pure metal and a compound.

The third group of alloys is comparatively rare, as very few of the metals are isomorphous. An example, however, is found in the case of the gold-silver alloys. The freezing-point curve consists of a single branch uniting the melting-points of gold and silver, and a microscopical examination fails to show the existence of any eutectic or any definite compound. The properties of the alloys pass gradually from those of gold to those of silver.

These three groups of alloys have been described as having normal curves of fusibility; but in a large number of alloys the curves are more or less complicated. For example, it may happen that one metal is only partially soluble in the other and is at the same time capable of uniting with it in different proportions to form a definite compound. Again, a compound may be partially soluble in the pure metal, or may be isomorphous with one of the metals. In such cases very complex freezing-point curves are obtained, whose meaning can only be explained by patient and laborious research. The alloys of copper and tin give rise to a complex freezing-point curve; and as these alloys have received more attention than any others, they may be considered as an illustration of the investigations which may be necessary in order to understand the constitution of a series of alloys.

Fig. 43 is the complete series of curves given by Heycock and Neville, and represents not only the results obtained from the cooling curves of the alloys, but also the results of a very thorough microscopical examination. In order to understand the changes which take place in the solid alloys which give rise to breaks in the cooling curves, Heycock and Neville have adopted the plan of quenching the alloys at temperatures above and below the breaks shown by the pyrometer, thus fixing the structure of the alloys at these temperatures, so that they can be examined under the microscope. A diagram which gives the temperature at which changes take place both in the solid and liquid alloys is known as an equilibrium diagram.

The curve ABCDEFGHIK is the freezing-point curve of the alloys, and has been described by Prof. Bakhuis Roozeboom as the *liquidus*, indicating that when the temperature is above this line the alloy is entirely liquid.

The line $\mathrm{AblcdefE_2E_3H'H''lK'}$ has similarly been called the *solidus* curve, indicating that at temperatures below this line the alloys are entirely solid. Between these two curves there is a region in which the alloys are partly liquid and partly solid. At these temperatures the alloys consist of a solid relatively rich in copper and a liquid relatively rich in tin.

The lines below the solidus curve indicate changes taking place in the solid alloys, and have been arrived at by a combination of pyrometrical and microscopical examinations.

Heycock and Neville recognise six constituents in the copper-tin alloys. These are—

The constituent α, which is a solid solution of tin and copper, containing not more than 9 per cent. of tin. The portions solidifying first consist of almost pure copper, leaving a liquid relatively rich in tin.

The constituents β and γ are also solid solutions of copper and tin, differing from each other in crystalline form. The β crystals

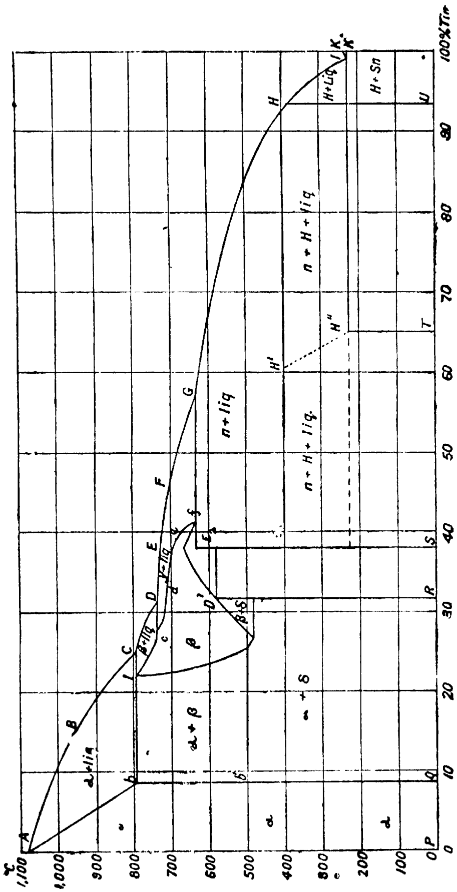

Fig. 43.—Equilibrium Diagram of Copper-tin Alloys.

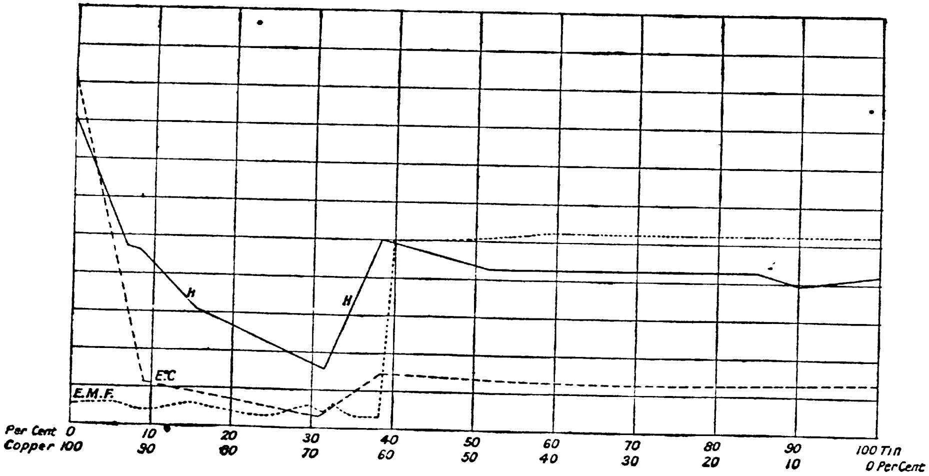

FIG. 44.—Physical Properties of Copper-tin Alloys.

H. Thermal Conductivity.
E.C. Electrical Conductivity.
E.M.F. Electromotive Force.

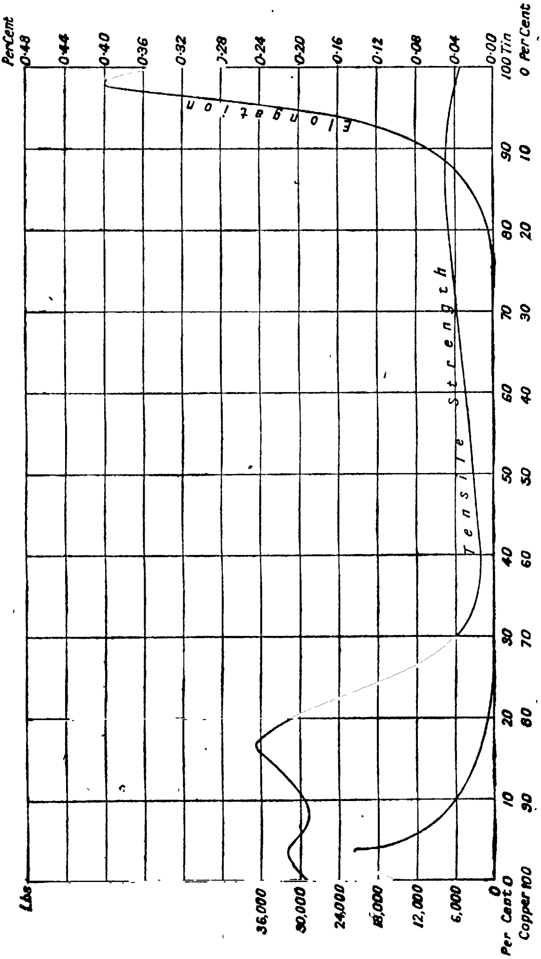

FIG. 45.—Mechanical Properties of Copper-tin Alloys.

contain from 22·5 to 27 per cent. of tin, and the γ crystals from 28 to 37 per cent. of tin.

These constituents may be described as transition constituents, as they are never found in a slowly-cooled alloy. They exist, however, at temperatures above 500° and in alloys quenched above that temperature.

The constituent δ is believed to be the compound Cu_4Sn. It is almost white in colour, and does not crystallise from the liquid alloy; it is only formed when the alloy cools below 500°.

The constituent E is the compound Cu_3Sn. It crystallises in plates, and is easily separated from the alloys.

The constituent H is the compound CuSn. In the slowly-cooled alloys containing from 40 to 90 per cent. of tin, this constituent is found bordering the crystals of Cu_3Sn, whereas in the alloys containing from 93 to 98 per cent. of tin it occurs in the form of hollow crystals, which Heycock and Neville have suggested may be due to the fact that the crystals have formed round nuclei of Cu_3Sn, and that the nuclei have subsequently been redissolved.

The temperatures at which these constituents are capable of existing are indicated in the diagram by lines which divide the lower part of the diagram into compartments. It is thus possible to see at a glance the constitution of any particular alloy at any temperature. Consider, for example, an alloy containing 15 per cent. of tin cooling from a molten condition. At 950° crystallites of almost pure copper separate out, and as the temperature falls these become richer and richer in tin until at a temperature just below 800° the constituent β solidifies, and the whole alloy is now solid. When the temperature falls below 500° the constituent β is no longer stable, and the alloy splits up into a mixture of α and δ, in which condition it remains at temperatures below 500°. A glance at the diagram will show that some of the alloys, especially those containing from 23 to 40 per cent. of tin, undergo very remarkable changes during cooling.

The constitution and properties of a series of alloys may be conveniently represented in the form of a chart, of which fig. 46 is a simple case. The curve at the top is the complete freezing-point curve of the lead-tin alloys, while the curve immediately below it shows their constitutional composition. Below this are

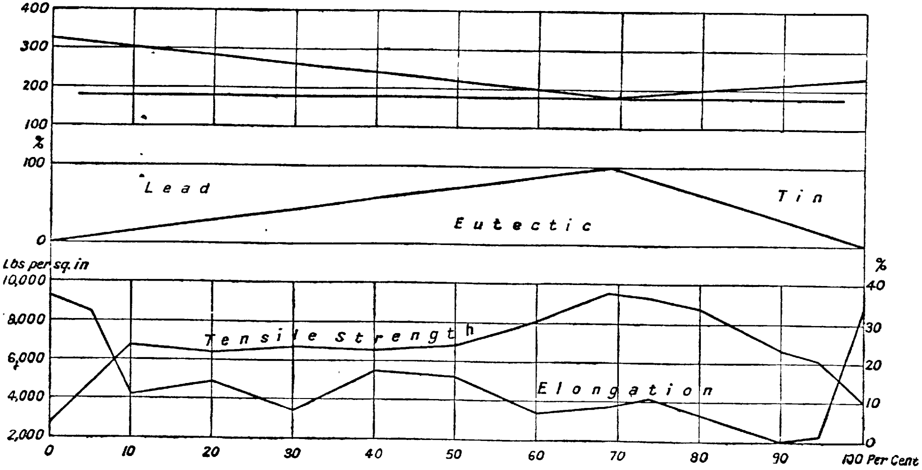

FIG. 46.—Alloy Chart of Lead-tin Alloys, showing—

1. Freezing-point curve.
2. Constitution.
3. Mechanical properties.

plotted the tensile strength and elongation, so that the mechanical properties corresponding to any structure or constitution can be seen at a glance.

From a theoretical point of view the subject of triple alloys has received a great deal of attention within the last few years. The first complete and systematic investigation was due to Charpy, who selected the alloys of lead, tin, and bismuth as being the simplest possible series of ternary alloys. The freezing-points of the three series of binary alloys, lead-tin, lead-bismuth, and tin-bismuth, have been determined in addition to those of the ternary series lead-tin-bismuth, and the results are plotted in the following manner. The composition of the alloys is represented graphically by means of an equilateral triangle ABC (fig. 47). The three vertices A, B, and C represent the three constituent metals, and any point on the sides corresponds to a binary alloy of the two metals at the extremities of the line. Ternary alloys are represented by points inside the triangle, and their composition by perpendiculars drawn from the point to the sides. Thus Ma represents the proportion of metal A; Mb the proportion of B; and Mc the proportion of C. Charpy describes his method thus: "In order to represent the variation of a certain property—the fusibility, for instance—a perpendicular is raised from each point to the plane of the triangle, and a distance is measured upon that perpendicular proportional to the temperature of fusibility of the alloy represented by the foot of the perpendicular. The *locus* of these points constitutes the surface of fusibility which corresponds to the curves of fusibility of binary alloys."

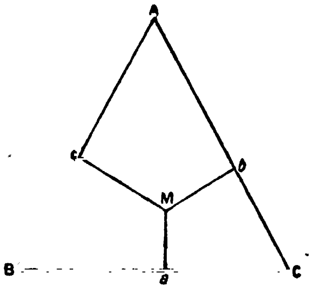

FIG. 47.—Triangular Diagram of Composition.

Charpy has constructed a model showing the surface of fusibility of the lead-tin-bismuth alloys, and has also plotted the isotherms of the surface of fusibility (fig. 48). In this diagram the surface of fusibility of lead, tin, and bismuth alloys is composed of three zones, which, by their intersections, give the lines Eε, E′ε, and E″ε, the points EE′ and E″ corresponding to the three binary eutectics of lead and bismuth, lead and tin, and tin and bismuth respectively. The point ε corresponds to the ternary eutectic containing

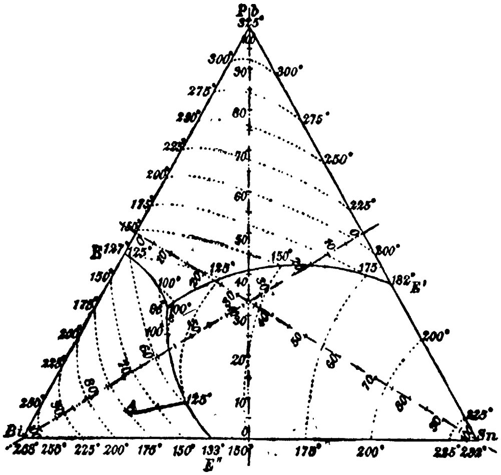

FIG. 48.—Surface of Fusibility of the Alloys of Lead, Tin, and Bismuth.

32 per cent. of lead, 15·5 per cent. of tin, and 52·5 per cent. of bismuth, and melts at 96°.

Alloys represented by points in the triangle lying above EεE′ will, on solidification, deposit lead first; and in the same way alloys represented by points lying between EεE″ and Bi and between E′εE″ and Sn will first deposit bismuth and tin respectively.

These results have been fully confirmed by the microscopical examination of the alloys.

Within recent years much has been written upon the constitution of alloys from a theoretical standpoint, and more especially from the point of view of the so-called Phase Rule first enunciated by Willard Gibbs. This rule states that—*it is necessary to assemble at least* n *different molecular species in order to construct a complete heterogeneous equilibrium consisting of* n + 1 *different phases.* At one particular temperature and pressure only is it possible to have $n+2$ phases in equilibrium. Thus, to take the simplest possible case, the compound H_2O is regarded as a simple molecular species and therefore $n=1$. Now, there are three possible phases in which this compound can exist, viz. ice, water, and water vapour; but according to Gibbs' phase rule only two $(n+1)$ phases can remain in equilibrium except at one critical point. Thus a condition of equilibrium extending over a certain range of temperature and pressure may be established between ice and water, water and water vapour, and ice and water vapour, but only at one temperature and pressure (0·0075° and 4·57 mm.) can the three phases occur together.

A more complicated case (which has, however, been thoroughly investigated by Roozeboom) is to be found in the conditions of equilibrium existing between water and sulphur dioxide. Here we have two molecular species $(n=2)$ and four possible phases, viz. :—

1 A solid hydrate $SO_2,7H_2O$.
2. A solution of SO_2 in water.
3. A solution of water in liquid SO_2.
4. A gas mixture of SO_2 and H_2O

It has been proved experimentally that only three $(n+1)$ of these phases can exist in a condition of equilibrium except at the critical point.

It is evident that the application of the phase rule may be extended to meet the case of alloys with the object of determining the number of possible constituents which can exist in a state of equilibrium in a given system; and this has been done by Roozeboom in the case of the iron carbon alloys The subject is, however, a complicated one, and can hardly be said to have added much to our knowledge of alloys. The student who wishes to follow it up should study the work of physicists (and more especially the masterly researches of Roozeboom) before attempting to deal with the theoretical conclusions of those who are less perfectly acquainted with the subject.

Relation between Constitution and Mechanical Properties.—The relation between the constitution and the mechanical properties of an alloy is clearly defined, and the subject is of so much importance in the industrial applications of alloys that it deserves the closest attention. Fortunately the number of constituents which may be present in an alloy is limited to four, viz. pure metals, solid solutions, compounds, and eutectics, and it is only necessary to consider the nature and properties of these constituents and their influence on the properties of an alloy.

Pure metals are relatively soft, malleable, and ductile, and when present in an alloy they tend to impart these qualities to it.

Solid solutions, as already stated, possess properties similar to those of pure metals. They are relatively soft, malleable, and ductile, and it may be pointed out that practically all the industrial alloys which are capable of being cold rolled, drawn, and spun consist of a single solid solution. Brass, bronze containing less than 8 per cent. of tin, malleable phosphor-bronze, coinage-bronze, aluminium-bronze containing less than 7·5 per cent. of aluminium, cupro-manganese, cupro-nickel, German silver, standard gold, magnalium, and some of the nickel and manganese steels, are examples of ductile alloys consisting of a single solid solution. Standard silver may be regarded as an exception to the rule, but the quantity of eutectic in standard silver is very small, and the silver-copper eutectic is much more ductile than most eutectics. Alloys consisting of two solid solutions are less ductile, but are still capable of being rolled and worked hot. Muntz metal, manganese-bronze, delta metal, and a number of other "special bronzes" and brasses, are examples of these alloys.

Compounds are harder than the metals of which they are composed, and brittle. They decrease the ductility of the alloy, and tend to lower its tensile strength. On the other hand, they increase the compressive strength of the alloy, a property which is of great importance in the case of bearing and antifriction metals, and at the same time they improve its working qualities as regards turning, filing, etc. The industrial alloys of this class include bronzes containing more than 8 per cent. of tin, cast phosphor-bronze, all the white metal antifriction alloys, and the aluminium alloys containing copper, nickel, or tin.

Eutectics are brittle, and possess lower melting-points than either of their components. Owing to this difference in melting-point the eutectic portion of an alloy separates between the crystals of the other constituent, forming a network or cement, with the result that the ultimate strength and ductility of the alloy are practically the same as those of the eutectic. It follows that alloys containing eutectics are, with one or two exceptions, unsuited for constructional work. Their principal employment is probably in the form of solders, in which the difference in melting-points of the constituents enables them to be manipulated while in a semi-fluid or pasty condition. The eutectic of iron and carbon known as *pearlite* is an exception to the rule and is unique, as it is formed after the steel is completely solid. The result of this is that the crystals of iron are not surrounded by eutectic, but the eutectic is itself surrounded by free iron; so that the formation of pearlite in steel is rather more comparable, as regards its influence on the mechanical properties, with the formation of compounds in other alloys. In order to distinguish a eutectic structure formed after solidification from those formed in the usual way, the term *eutectoid* has been applied to it.

Alloys containing eutectics are sometimes rendered useful by chilling or cooling them rapidly, so that the eutectic is not permitted to solidify between the crystals, but is evenly distributed throughout the mass of metal. Here, again, the eutectic plays the part rather of a compound than that of a normal eutectic.

So far we have only considered alloys of two metals or binary alloys; but when we come to triple alloys the difficulties are not greatly increased, for we find that the alloys contain, as before, only solid solutions, compounds, and eutectics. It is true that a solid solution of three metals may differ in hardness, strength, or ductility from a solution containing only two, and it is equally true that a eutectic of three metals has a lower melting-point than a eutectic containing two, but the general characteristics of the constituents are the same. Solid solutions are the ductile constituents; compounds are the hard and brittle constituents; eutectics are hard and brittle and tend to solidify between the grains of the alloy, thus ruining its ductility.

It is evident, therefore, that the study of the structure and constitution of alloys is of the utmost importance in enabling a clear understanding to be gained of the influence of additions and impurities on the mechanical properties of metals. As examples of the various ways in which the mechanical properties of a metal may be affected by the addition of another metal (or non-metal) let us take the case of a metal, copper, to which zinc, aluminium, tin, phosphorus, lead, and bismuth are added respectively.

1. *Zinc.*—When zinc is added to copper the tensile strength and elongation gradually increase until 30 per cent. of zinc is reached, but beyond this there is a decrease in the ductility of the alloys as shown by the elongation. With 40 per cent. of zinc the alloys can still be rolled hot, but with further additions the falling off in ductility is so rapid that they are of no use for constructional purposes. An examination of the structure of these alloys reveals the fact that 30 per cent. of zinc is soluble in copper, forming simple homogeneous solid solutions, whereas with more than 30 per cent. a second constituent makes its appearance, and as the proportion of this second constituent increases so the ductility of the alloy decreases.

2. *Aluminium.*—As in the case of zinc, the addition of aluminium to copper raises the tensile strength and elongation, but in this case the maximum elongation is reached with only 7 per cent. of aluminium, and beyond this the falling off in ductility is so rapid that the alloys with more than 10 per cent. of aluminum are practically useless. The structure of the alloys shows that only about 7 per cent. of aluminium is dissolved by copper with the formation of homogeneous solid solutions, and with more than this amount a second and extremely hard constituent makes its appearance.

3. *Tin.*—With tin the falling off in ductility is very rapid, the maximum elongation being reached with less than 5 per cent. of tin. This is explained by the fact that although copper is capable of dissolving 8 per cent. of tin, the solid solutions so formed are not homogeneous, the first portion of the alloy to solidify being almost pure copper and the last portion containing most of the tin. Hence the maximum ductility is obtained with much less than 8 per cent. of tin. The properties of the alloys may be modified to some extent by heat treatment, but for the moment we are only considering the naturally cooled or cast alloys.

4. *Phosphorus.*—A small fraction of 1 per cent. of phosphorus in copper is sufficient to completely destroy its ductility, and the reason for this is obvious if we consider the constitution of the alloys. Phosphorus combines with copper to form a well-defined

compound, corresponding to the formula Cu_3P, which does not crystallise out by itself when the alloy cools, as is commonly the case with such compounds, but forms a eutectic with a further portion of the copper. Now it must be remembered that it is not the percentage of phosphorus which influences the mechanical properties of the copper, nor even the percentage of phosphide of copper, but the percentage of eutectic; and when we consider that 1 per cent. of phosphorus is equivalent to more than 12 per cent. of eutectic, and that this eutectic which melts at 705° solidifies between the crystals of copper, it is not difficult to understand how a small quantity of phosphorus can exert such a marked influence on the mechanical properties of the copper.

5. *Lead.*—Lead does not alloy with copper but separates out in the form of minute globules of metallic lead. In this condition it has a relatively small effect on the strength of the metal. Moreover, the specific gravity of lead being considerably higher than that of copper renders its influence still smaller, for it is important to note that the mechanical properties of an alloy are governed by the *volume* of the constituents and not by their *weight.* Hence, comparing the influence of 1 per cent. by weight of lead and phosphorus, we find that the constituents affecting the mechanical properties of the metal are 0·8 per cent. in the case of lead and 12·1 per cent. in the case of phosphorus. The relatively small influence of lead on copper and its alloys is shown by the remarkable strength of the so-called "plastic bronzes," which often contain as much as 30 per cent. of lead. It is obvious, however, that this only applies to the metal in a cast state, as copper or bronze containing a constituent melting at as low a temperature as 327° cannot be worked to any appreciable extent.

6. *Bismuth*, like lead, does not alloy with copper, but unlike lead it does not separate as isolated globules but forms a thin network or film between the crystals of copper. It follows that anything above a trace of bismuth in copper renders it too brittle to be of any use.

From a consideration of the foregoing examples it will be seen that the influence of an added metal on the mechanical properties of a metal or alloy depends on (*a*) the condition in which it exists, *i.e.* whether it remains free or enters into chemical combination, (*b*) the shape or form it assumes, and (*c*) its volume.

These questions are of vital importance when dealing with the influence of impurities, for it sometimes happens that an alloy may be perfectly good or absolutely useless according to the chemical or physical condition of a certain impurity. Moreover, the presence of such impurities is occasionally unavoidable, and the problem then presents itself of finding some means by which they may be rendered harmless, or at least as little harmful as possible. This may sometimes be effected by heat treatment and sometimes by the addition of a second impurity which, by combining with the first, causes it to assume a different and less injurious form. As an example of the change brought about both in the chemical and physical condition of an impurity by heat treatment we may take the case of steel castings. In these a portion of the silicon present combines with the manganese and sulphur to form a silico-sulphide which separates between the crystals of iron and induces brittleness in the metal. On annealing, however, the compound is decomposed, the silicon passing into solid solution with the iron and the manganese sulphide aggregating or balling up into isolated globules which may be regarded as practically harmless in a casting. The change in structure is illustrated in photographs 56 to 59.

An example of change in form induced in an impurity by the addition of a second impurity is also to be found in the best known of all alloys, steel. In the early days of the Bessemer process it was found that the steel produced was of little use owing to its brittleness, and it was not until Mushet suggested the addition of manganese to the molten metal that good steel was obtained and the process became a commercial success. The explanation of the difficulty is now perfectly clear. The sulphur in the steel combines with part of the iron to form sulphide of iron, and this compound having a low melting-point separates out between the crystals of iron (just as bismuth separates between the crystals of copper as already noticed), giving rise to a brittle metal. Manganese, however, has a greater affinity for sulphur than iron, and forms a sulphide whose melting-point is very much higher than that of iron sulphide. The result is that instead of having a brittle constituent separating between the crystals of iron, isolated crystals or globules of manganese sulphide are formed which are to all intents and purposes without influence on the properties of the steel as regards its suitability for rolling or forging. But it must not be supposed that manganese sulphide is an entirely harmless constituent of steel. In large sections it may be so, but at the same time it is responsible for many troubles, including the corrosion and pitting of boiler plates.

At the temperature at which steel is rolled the manganese sulphide is in a plastic condition and follows the rolling in the same proportion as the steel. Thus in thin steel sheets it also occurs in thin sheets or laminæ, and if such sheets are subjected to severe bending or stamping the sulphide sheets form planes of weakness and the metal gives way. Photograph 47 shows these sheets or flakes of sulphide in section in a piece of rolled steel, and here again its influence is due to the shape or form in which it occurs.

Cases of the elimination of a eutectic structure by the addition of a second impurity are to be found in the addition of tin to copper containing phosphorus, and in the addition of arsenic to copper containing oxygen. These are shown in photographs 48 to 55, and are considered in another chapter.

Numerous examples occurring in everyday practice might be quoted, but those already referred to will serve to show the importance to the practical man of a study of the structure and constitution of alloys. It throws a new light on the subject, and explains the relation between composition and mechanical properties in a way that chemical analysis by itself is incapable of doing. In fact, it interprets the results of chemical analysis, for until recently chemical analysis as applied to metals and alloys has been much less satisfactory than in other branches of science. In the analysis of nearly all materials it has long been recognised that a simple statement of the percentage of the elements present is not sufficient, but that it is necessary to go a step further and determine the condition in which these elements occur. What we may describe, therefore, as a constitutional analysis gives the actual constituents which go to make up the body under examination, whereas an ultimate analysis only gives the elements in that body regardless of the way in which they are combined. Nevertheless, it is not the ultimate components but the constituents which govern the mechanical and physical properties of an alloy, and an ultimate chemical analysis gives us no insight into its properties, except in so far as we have learned by long experience to associate a certain analysis with certain properties. Only in one instance does the chemical analysis of an alloy make any distinction between the different modes of occurrence of any constituent, viz. in the case of cast iron, in which it is customary to distinguish between the free carbon or graphite and the combined carbon. But carbon is not the only element which may exist in more than one form. Silicon, for example, may exist as silicate or may enter into solid solution with the iron; and whereas relatively large quantities in solution are not only harmless but often beneficial, quantities of silicate as small as 0·03 per cent. are objectionable if not actually dangerous. It has been stated by Capt. Howorth that in the case of heavy nickel steel gun forgings, 35 per cent. of the test pieces from the breech end and 5 per cent. from the muzzle end showed silicate defects in the fracture. In spite of the fact that 0·03 per cent. of silicate may cause the rejection of the steel, the specification allows 0·05 to 0·20 per cent. of silicon, and chemical analysis fails to distinguish whether this is present as silicon or as silicate.

The structure of an alloy must be governed by the purpose for which it is intended. Mere mechanical strength is in many cases not the only, or even the most important, factor, and inability to realise the importance of structure has often led to unexpected failure. An instance of this has been quoted by Mr Archbutt in connection with the manufacture of slide valves on the Midland Railway. These are made of bronze containing about 15 per cent. of tin, and are tested by putting them under a falling weight of 112 lbs. with a blunt knife edge. The valves are cast in sand, and when supported on 9-inch centres a single blow from a height of 8 feet is sufficient in most cases to crack them, while three blows from the same height will break them in half. If, however, the castings are quenched from a temperature just above 500°, they will stand four blows before cracking and about nine blows before breaking. In some cases fifteen blows from a height of 8 feet and three blows from a height of 10 feet were required to break them. Owing to their unusual strength and toughness the practice of quenching the castings was adopted, but soon had to be abandoned owing to the rapid wear of the valves. The explanation is simple. The cast alloys consist of particles of a hard constituent embedded in a softer matrix—a characteristic and essential structure of all alloys required to resist friction or abrasion. The quenched alloys, on the other hand, possess a homogeneous structure which is ill adapted to resist wear.

Another case in which too much importance given to mechanical tests instead of to structure and constitution led to failure in practice occurred in the use of an alloy containing 9·8 per cent. of aluminium and 1·9 per cent of manganese for slide valves. Tests on this alloy recorded in the Ninth Report to the Alloys Research Committee of the Institution of Mechanical Engineers showed remarkable results, but a trial of the alloy in the form of locomotive slide valves showed that they tore the cylinder face away, and they had to be taken out after 5800 miles' service.

Such experiences afford convincing proof of the importance of structure on the properties of alloys in service. That the subject is no longer of purely theoretical interest, but is recognised by practical men as being of real importance to them, may be gathered by the remarks of Mr George Hughes, Chief Mechanical Engineer to the Lancashire and Yorkshire Railway, who says: "The success of a bearing metal alloy depends more upon structure than absolute composition, the proper distribution of a number of the tin-antimony crystals in a softer matrix of tin or lead being essential."

CHAPTER V.

INFLUENCE OF TEMPERATURE ON THE PROPERTIES OF ALLOYS.

IT frequently happens that metals and alloys are used at temperatures either above or below the normal atmospheric temperature, and it is of considerable importance to know how the metal will behave under these abnormal conditions. The influence of high temperatures is perhaps of greater practical importance than that of low temperatures; but at the same time the results obtained by Dewar, Hadfield, and others at low temperatures are of the greatest value. The available data relating to the subject are not numerous, and in many cases the results are conflicting. Moreover, in some cases the results obtained in actual practice have not been in accordance with those obtained experimentally. The explanation of these discrepancies is probably to be found in the fact that the alteration in the properties of a metal or alloy due to variations in temperature is not always of the same nature, and before dealing with experimental results we may with advantage consider the possible changes which may be brought about in a metal by a variation in temperature.

In the first place, with an increase in temperature and consequent increase in molecular activity, we should expect a gradual and regular falling-off in the tensile strength until, in the neighbourhood of the melting-point, the tenacity becomes *nil.* Moreover, this change should be common to all metals, and experimental proof of it is not lacking. Thus Dewar has shown that at - 182° mercury has a tenacity about half that of lead at the ordinary temperature, and iron, copper, nickel, aluminium, etc., exhibit a marked increase in tensile strength at the same low temperature. The following figures show the tensile strength and elongation of copper at temperatures between − 182° and + 530°, the first two results being those of Hadfield and Dewar, and the remaining figures those of Le Chatelier. The two results at normal temperature are sufficiently close to justify the figures being regarded as a single series of observations (the small difference being due to the fact that Le Chatelier employed a purer sample of copper and in a completely annealed state), and they may be taken as representing the normal behaviour of a pure metal or a homogeneous solid solution.

MECHANICAL PROPERTIES OF COPPER AT VARYING TEMPERATURES

Temperature.	Tensile strength. Tons per sq. in.	Elongation.
− 182	23	45
+ 15	15	42
15	14·7	47
110	12·9	41
200	11·4	36
330	9·6	34
430	8·1	17·8
530	4·6	16·4

Normal behaviour, such as that exhibited by copper, is comparatively rare, and we have now to consider abnormal behaviour, which may be due to—

1, An allotropic change in the metal taking place suddenly; 2, a molecular change taking place slowly; 3, a heterogeneous structure.

1. **Allotropic Change.** — Examples of allotropic changes accompanied by changes in the physical properties taking place in metals are not uncommon. Thus iron undergoes a change at 760° and also at 860°, the three varieties of iron being described by Osmond as α iron, existing at temperatures below 760°; β iron, existing between 760 and 860°; and γ iron at temperatures above 860°. α iron is soft and magnetic, β iron is non-magnetic, and γ iron is hard and non-magnetic. Nickel undergoes a change at an even lower temperature, viz. 300°, above which temperature

it ceases to be magnetic. Zinc is brittle at the ordinary temperature, but at 150° it becomes malleable, and again loses this property at higher temperatures. Tin at low temperatures, but not lower than those reached in cold climates, undergoes a molecular change and falls to powder. Such changes are abnormal, and it is not yet known except in the case of iron to what extent these changes may take place in the metals when alloyed.

2. **Gradual Molecular Change.** — Some metals and alloys undergo a gradual change in their crystalline character, which is greatly accentuated as the temperature is raised. The change may be simply an increase in the size of the crystals, or may even be a change in the crystalline form. As an example of the gradual growth of crystals we may take the case of brass containing 70 per cent. of copper, and aluminium bronze containing less than 8 per cent. of aluminium. If these alloys are annealed at comparatively low temperatures the crystals develop in size and there is a marked falling-off in the mechanical properties. This growth of crystal will be referred to later.

3. **Heterogeneous Structure.**—Alloys containing two or more constituents are more liable to suffer deterioration at high temperatures than those containing only one constituent, especially if one of the constituents is a eutectic. The eutectic having a melting-point often very much lower than the constituent metals, is affected at a correspondingly lower temperature; and if the eutectic forms, as is frequently the case, a network or cement round the grains or crystals of the alloy, the strength of the eutectic represents the strength of the alloy. An example of this is found in copper containing bismuth.

Considering these three causes of deterioration it will be seen that one of them, the second, would not occur until after the lapse of some time, and this is sufficient to explain the failure in actual practice of alloys which had given excellent results when merely tested at high temperatures. It is therefore important to note that mechanical tests carried out at high temperatures are not sufficient to indicate the behaviour of the metal in practice.

The most complete series of experimental results yet published has been obtained by Bengough, who has extended his tests to higher temperatures than previous observers. He finds that both in the case of pure metals and alloys there is a gradual decrease in tensile strength as the temperature rises until a definite temperature is reached, beyond which the decrease takes place more slowly but still uniformly. This critical temperature he describes as the "temperature of recuperation," and the point at which the change takes place he calls the "mechanical critical point." The curve representing the tensile strength of aluminium shown in fig. 49 is similar to that of copper and all the copper alloys upon which tests were carried out Beyond the critical point there is a rapid increase in the elongation until the temperature approaches the melting-point of the metal, when it shows a sudden drop. In many cases the metals give out a "cry" when tested above the critical temperature similar to that of tin.

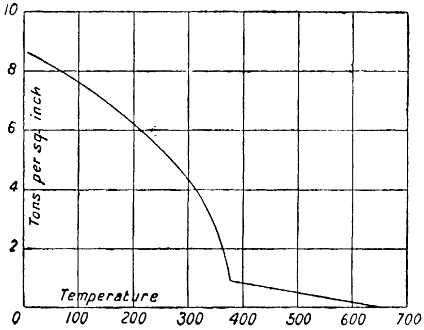

FIG. 49.—Tensile Strength of Rolled Aluminium at High Temperatures.

Bengough points out that there is a marked difference between the curves representing the tensile strength of cast metals and those which have been worked at comparatively low temperatures. Although both show the critical point, their behaviour at temperatures below this point is different. In the case of cast metals, the decrease in strength varies directly with the rise of temperature, and the curve is therefore a straight line, whereas in the case of worked metals the decrease in strength is more rapid as the temperature rises. The two types of curve are illustrated in fig. 50.

The following table gives the critical temperatures of a number of metals and alloys :—

Metal or Alloy.	Critical Temperature.	Tensile Strength at Critical Temperature Tons per sq. in.
Copper	650°	1·3
Aluminium	395	0 9
Cupro-nickel (20 per cent. nickel)	710	3·0
Brass (30 per cent. zinc) . .	440	2·5
,, (40 ,, ,,) . .	430	5·0

These critical points are undoubtedly of great theoretical interest, but from the practical point of view the metals have ceased to be of any use long before these temperatures are reached.

Alloys used for Firebox Stays.—One of the most important applications of metals and alloys at high temperatures occurs in firebox plates, and more especially firebox stays; it is in this connection that most of the work on the strength of alloys at high temperatures has been carried out, and attention has been particularly directed to the alloys of copper. The mechanical requirements of a metal suitable for firebox stays are that it can be easily worked and riveted, and that it shall be as soft as, or softer than, the copper plates into which they are riveted. The alloys examined include bronze, phosphor-bronze, manganese-bronze, aluminium bronze, brass, copper-nickel alloys, and mild steel. The behaviour of these alloys will be briefly considered. As regards the temperature actually reached by the plates and stays there is a considerable difference of opinion, and it is difficult to arrive at any conclusions from experimental data. Webb has measured

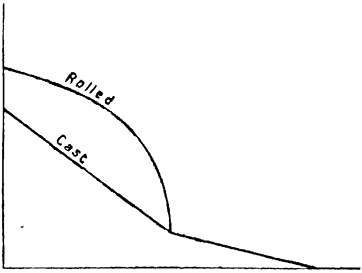

FIG. 50.—Tensile Strength of Cast and Rolled Metals at High Temperatures.

the temperature of the centres of a number of firebox stays by drilling a hole through the centre of the head and inserting a thermo-couple. The results showed that at a distance of 2 ins. from the furnace end the temperature varied from 170° to 175° in a boiler working at 120 lbs. pressure, steaming heavily and blowing off, while at a distance of half an inch from the furnace end the temperature rose to 215° to 230° under the same conditions. An attempt to determine the temperature of the surface of the copper plate and of the ends of the stays inside the firebox, in the vicinity of the brick arch, gave temperatures of 540° and 615° respectively. It must be remembered, however, that there is intense local heating, and it is no uncommon thing to see the surface of the copper plate showing drops of copper where the metal has been actually melted. It is difficult, therefore, to say what temperatures are actually reached, but it may be taken that the stays reach a temperature of at least 200°, and probably considerably more.

Bronze.—The only alloys of the copper-tin series available for the purpose of firebox stays are those containing less than 8 per cent. of tin (that is to say, those consisting of a solid solution of tin in copper), and these are probably the least satisfactory of any alloys. Their mechanical properties fall off rapidly at about 200°, a bronze giving a tensile strength of 11 tons per sq. in. at 200° falling to 7·8 tons at 260°.

In an actual test carried out by Webb, the boiler of a six-wheel-coupled goods engine working at 150 lbs. per sq. in. was fitted with bronze stays containing 3 per cent. of tin. After running 93,290 miles 145 stays had to be removed as defective, and the average rate of renewal worked out at one stay per 791 miles.

Phosphor-Bronze. — The phosphor-bronzes possessing the mechanical properties suitable for firebox stays are those containing small percentages of tin and only traces of phosphorus. In fact, the phosphorus merely acts as a deoxidiser, and produces a better class of bronze than that obtained by ordinary melting. Data relating to the properties of phosphor-bronze at high temperatures are scarce, but it is probable that they would possess distinct advantages over ordinary bronze.

Aluminium-Bronze.—The alloys of aluminium and copper containing less than 8 per cent. of aluminium possess the required qualities necessary for firebox stays, but they deteriorate very rapidly at high temperatures. A bronze containing 7·1 per cent. of aluminium, which showed a tensile strength of about 25 tons per sq. in. with an elongation of 89 per cent. on 2 ins. at the ordinary temperature, gave only 9 tons per sq. in. and 14 per cent. elongation at 400°.

An actual test carried out by Webb under the same conditions as those described in the case of the copper-tin stays gave disastrous results. The alloy contained 7 per cent. of aluminium, and after being in use only two months and running 2400 miles, the engine had to be taken off the line owing to the number of breakages.

Le Blant also states that the alloys of copper and aluminium are the most sensitive to an increase in temperature, and these practical results are the more remarkable, inasmuch as Charpy describes the aluminium-bronzes as being superior to other copper alloys. The explanation of this discrepancy is to be found in the fact that aluminium-bronze (containing less than 8 per cent. of aluminium) is one of those alloys which undergo a gradual change on heating. At a temperature of 180° (and possibly lower) the crystals increase in size until they reach very large dimensions, and the growth of the crystals is accompanied by a falling-off in the strength of the alloy. Photographs 28, 29, 30, and 31 show the changes which take place in the structure of aluminium-bronze, the alloy represented being the actual material used in Webb's experiments. No. 28 is the original material as supplied. Nos. 29 and 30 represent the same sample after prolonged heating at a low temperature. No. 31 is the same sample heated to a higher temperature, but still below its melting-point. Test pieces of the alloy showing large crystals, as in photograph 30, give low tensile tests and show a curious crinkling of the surface over the whole length of the specimen.

Brass.—Copper-zinc alloys of varying composition may be used for firebox stays, the percentage of zinc varying from 0 to about 40. Those containing less than 10 per cent. of zinc appear to give fairly good results in practice. Thus, in Webb's experiments, a locomotive boiler working under the same conditions as those previously described, and fitted with stays made of brass containing 90 per cent. of copper and 9 per cent. of zinc, gave results equivalent to a renewal of one stay per 5588 miles. The renewals were mostly due to wasted heads and leakage, rather than actual breakage. Alloys containing a higher percentage of zinc but not exceeding about 30 per cent. (that is to say, those consisting of a single solid solution) show a decided falling-off in strength with an increase in temperature.

Brasses containing about 40 per cent. of zinc, consisting of two constituents, both solid solutions, give very poor results. Webb found that an alloy containing 40 per cent. of zinc gave results equivalent to one stay renewed per 262 miles only.

Copper-Arsenic Alloys.—In this country copper containing arsenic up to 0·5 per cent. is more widely used than any other alloy for firebox stays. Owing to its low initial cost it has had few competitors until recently, but other alloys are now being used, and it is probable that the copper-arsenic alloys will be much less used in the future than they are at present.

Copper-Nickel Alloys.—Copper containing up to 5 per cent. of nickel has been used for firebox stays with good results. The alloy maintains its strength very well at high temperatures, and it has been stated that it fulfils all the requirements of a satisfactory and reliable stay material. Unfortunately the results obtained in actual practice have not been published, but an alloy containing 2 per cent. of nickel is used to a considerable extent, and Sir Gerard Muntz has stated that when engineers have once used this alloy they rarely return to the use of copper-arsenic alloys. The alloy is only slightly affected by extremely low temperatures.

Manganese-Bronze.—An alloy consisting of about 96 per cent. copper and 4 per cent. manganese, which is sometimes referred to as cupro-manganese, but sold commercially as manganese-bronze, is now very largely used, both in this country and abroad, for firebox stays. In a report submitted to the Congrès International des Méthodes d'Essais des Matériaux de Construction on locomotive firebox stays, Le Blant states that the metal which he has found least sensitive to heat is cupro-manganese. He concludes: "As the matter stands at present, the metal giving the least number of breakages is cupro-manganese. But it behaves badly under the action of the flames. It ought, therefore, to be reserved for the lines of stays which break most frequently, and as far as possible from the fire." This suggestion is carried out, and the following results obtained in actual practice, which are due to

M. du Bousquet of the Northern Railway of France, are of considerable interest.

Twenty locomotives were fitted with cupro-manganese stays in the upper three horizontal rows of the side plates and the back plate, the remaining stays being copper. Each firebox had 185 cupro-manganese stays and 986 copper stays, and the boiler pressure was 213 lbs. per sq. in. In four years only six breakages of cupro-manganese stays occurred, while 1875 copper stays were broken. In spite of the fact, therefore, that the cupro-manganese stays were placed in positions where it was known that breakages were most likely to occur, the breakages of copper stays were 58·6 times as frequent as breakages of cupro-manganese stays. Another set of twenty-five locomotives were fitted entirely with cupro-manganese stays, each firebox containing 1163 stays, and at the end of twelve months only one stay had had to be replaced. In another set of twenty locomotives cupro-manganese stays had been fitted in the upper three rows and in the corners of the side plates, each firebox containing 190 cupro-manganese stays and 973 copper stays. At the end of twelve months' running no cupro-manganese stay had failed, while 232 copper stays had had to be replaced.

Cupro-manganese stays have been used for some years by the Northern Railway of France, the Southern Company of France, and the Hungarian State Railways. The results appear to have been perfectly satisfactory, and the same alloy is now very largely used, but its employment in this country is of more recent date. A cupro-manganese, however, under the name of crotorite has been manufactured for some time past by the Manganese Bronze and Brass Company. At very low temperatures (– 182°) cupro-manganese shows an increase in tenacity and ductility, and Le Blant's statement, that of all the copper alloys cupro-manganese is the least affected by change in temperature, appears to be amply justified.

A number of tests on alloys for firebox stays have been made by Hughes at the Horwich works of the Lancashire and Yorkshire Railway, and the results, together with the analyses of the alloys, are given in the accompanying tables. The alloys were tested after heating for ten hours at 750° in the laboratory and also after nine hours in a locomotive firebox.

COMPOSITION OF ALLOYS.

Mark.	Description.	Analyses.									
		Copper.	Nickel.	Tin.	Lead.	Arsenic.	Bismuth.	Phosphorus	Manganese.	Iron.	Combined Oxygen.
A	Phosphorised, 1 inch . . .	99·8	trace	...	trace	0·12	..	0·06	...	trace	...
B	Phosphorised, 1$\frac{1}{16}$ inches . .	99 9	...	..	0·03	trace	...	0·05	...	0·01	...
C	Copper-manganese	90·4	...	...	...	...	...	...	7·78	1·82	...
E	High arsenic	99·3	0·05	..	0·07	0·48	...	...	..	...	0·11
P	„ arsenic	98·94	0·05	...	0·09	0·87	...	...		0·05	..
H	„ tensile	99·7	0·01	...	trace	0·20	...	0·04	...	0·03	trace
N	Copper-nickel	98·05	1 92	. .	...	trace	...	0·09		...	...
F	Copper to L. and Y. specification .	99·4	0·04	0·03	0·05	0·45	...	.	...	...	0·07

MECHANICAL TESTS.

Mark.	Description.	As Received (Annealed).				Heated Ten Hours at 750° C. (in Laboratory).				Heated Nine Hours in Locomotive Firebox.			
		Tensile tons per sq. in.	Elongation per cent. in 8 ins.	Contraction per cent.	Fracture.	Tensile tons per sq. in.	Elongation per cent. in 8 ins.	Contraction per cent.	Fracture.	Tensile tons per sq. in.	Elongation per cent. in 8 ins.	Contraction per cent.	Fracture.
A	Phosphorised, 1 in. .	14·3	57	81	Silky fibrous .	14·7	58·9	79·3	Fibrous distressed	14·6	51	79	Fibrous distressed
B	Phosphorised, 1$\frac{1}{16}$ ins.	14·8	52	79·9	,, fibrous .	14·7	67·3	83·6	,, red	14·6	49	94	,, ,,
C	Copper-manganese .	25·1	29	57·6	Brown dark fibrous	24·7	35·5	57·3	Brown dark fibrous	24·5	36	60·6	Fibrous
E	High arsenic . .	14·7	50	59·4	Silky fibrous .	14·6	48·5	55·1	Fibrous glossy	14·5	45	60·6	Fibrous distressed
P	,, arsenic . .	15·8	54	78·4	Spiral fibrous .	15·3	53·0	77·2	Fibrous brown distressed.	15·5	53	79	,, ,,
H	,, tensile . .	15·2	53	77·3	,, ,,	15·5	54·3	76·8	Spiral fibrous	14·5	45	75	,, ,,
N	Copper-nickel . .	15·2	49	78·2	,, ,,	16·1	43·0	75·2	Silky conchoidal	17·1	48	83	,, ,,
F	Copper to L. and Y. specification.	15·4	52	63·5	Silky fibrous .	...	...	...	...	15·0	46	60·6	Fibrous

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CHAPTER VI.

CORROSION OF ALLOYS.

In spite of the fact that the influence of corrosive liquids on metals and alloys is an important problem in many industries, there is very little available information on the subject. This is probably due partly to a widespread reluctance to publish the results of practical experience, and partly to the difficulties of experimental investigation. It is obvious that experimental tests can seldom reproduce the conditions which obtain in practice, but it is nevertheless possible to obtain comparative results which are of considerable value.

The process of corrosion may take place in several ways. The simplest of these may be described as chemical corrosion—that is to say, the alloy is merely dissolved in the liquid in the same way that a simple metal is dissolved in acid, such as zinc in sulphuric acid.

A more complicated process of corrosion occurs in the combined influence of a corrosive liquid and the atmosphere. This is of very common occurrence, and is frequently observed in the case of copper alloys, the maximum effect of the corrosion taking place at the surface of the liquid or when the metal is alternately immersed in the liquid and exposed to the air. An example of this is seen in the corrosion of brass by salt water. When totally immersed the corrosive action is slow, but in the presence of the atmosphere oxychloride of copper is produced, and rapid corrosion of the brass takes place.

Perhaps the most interesting and the commonest type of corrosion is that which may be described as electro-chemical. This occurs when two bodies possessing different electrical properties are immersed in contact with one another in a corrosive or conducting liquid. Owing to the difference of potential between the two bodies an electromotive force is set up, or, in other words, a galvanic battery is formed, and one of the bodies passes rapidly into solution. For this reason metals and alloys of different properties must not be placed in contact under liquids. Here we are dealing with two metals or alloys in contact, and the case is comparatively simple; but it follows that the same action will take place in a single alloy if it is not homogeneous in structure. For example, an alloy whose constituents separate out on cooling, or form compounds which separate on cooling, will almost certainly be rapidly corroded on account of the difference of electrical potential between the constituents. Hence alloys forming solid solutions are usually better able to resist corrosion than non-homogeneous alloys. Impurities due to the improper treatment of the alloy, such as dross, slag, oxides, etc., behave in a similar manner. Thus in the case of copper alloys the presence of copper oxide is particularly injurious, and the oxychloride of copper formed by the action of air and sea water on copper alloys accelerates corrosion in the same way. The influence of impurities on corrosion has received more attention in the case of metals than in the case of alloys, and it is well known that many metals in a pure state are only soluble with difficulty in acids, whereas the same metals in an impure state are readily soluble in the same acids. Unfortunately one of the most injurious impurities is usually overlooked in spite of the fact that it is of common occurrence. Oxygen in the form of metallic oxides and oxidation products is liable to occur in nearly all metals and alloys, and is a frequent cause of local corrosion and pitting. That it has not received more attention in this connection is probably due to the fact that its presence is not indicated in the results of an ordinary chemical analysis. Copper is the one exception in which oxygen is ever determined.

Metallic oxides appear to be practically insoluble in solid metals, and occur as particles varying in size and distribution entangled in the metal. Photographs 54 and 55 are taken from an etched and unetched section of a locomotive firebox plate, and will serve to illustrate the appearance of oxides (in this case copper oxide) under the microscope. The importance of the effect of these oxide particles on the corrodibility of the metal can hardly be over-estimated. On immersion in a corroding liquid each particle forms a small galvanic couple with the surrounding metal and becomes the starting-point of a "pit."

The differences of potential between metals and their oxides have been insufficiently studied, but it is probable that in nearly all cases they are of much greater importance than the differences of potential between the metallic constituents of a non-homogeneous alloy. The ordinary electric accumulator or secondary battery may be taken as an example of the practical application of the difference of potential between a metal and its oxide; and an example of the influence of an oxide on the rate of corrosion is to be found in the well-known fact that when the protective oxide coating on steel is partially removed corrosion of the unprotected steel is greatly accelerated.

Experimental results on the influence of oxides on the rate of corrosion are scarce, but a series of tests carried out by the author and extending over several years may be of some interest. A number of steel plates rolled from ingots which had been carefully deoxidised by the addition of silicon, and a number of plates rolled from the same steel made in the usual way, were exposed to the London atmosphere and at the end of every six months they were carefully cleaned and weighed. The experiments were repeated on different makes of steel, and in each case the result showed that the corrosion of the ordinary plates was greater by 24 per cent. than that of the deoxidised plates. It is evident, therefore, that the difference in corrodibility between a well-made alloy and the same alloy badly made may be greater than the difference between two alloys of different composition, and unless these facts are taken into consideration the results of comparative experimental tests may be very misleading.

In some cases the process of corrosion stops itself automatically by the production of compounds which hinder further corrosion. Cases of this description are not uncommon, and an example of the greatest importance occurs in the employment of lead pipes for carrying water. It is well known that lead is appreciably soluble in water, and to such an extent as to render the water unfit for drinking purposes. Moreover, nearly all waters contain considerable quantities of sulphuric acid in the form of sulphates, which also have a corroding action on lead; but the product of the corrosion in this case is a practically insoluble compound, lead sulphate, which forms a coating on the surface of the metal and effectually prevents further corrosion, either by sulphates or by the water itself.

Similar incorrodible coatings are formed on certain alloys, and an interesting example may be cited to illustrate this and also another protective influence exerted by one metal upon another. This is found in the case of an alloy of gold and silver containing 50 per cent. of each metal, which is practically insoluble in the ordinary acids. In hydrochloric acid or aqua regia a coating of silver chloride is immediately formed, and all action ceases. In nitric acid the silver on the surface is dissolved, and the alloy is then protected by a coating of gold which prevents further action taking place. This fact is well known to all assayers and refiners, and in the operation of "parting" bullion (*i.e.* dissolving out the silver with acid) it is necessary that the amount of silver should be considerably in excess of the gold, or the parting is incomplete. Certain copper alloys behave in a similar manner, the alloying metal being dissolved out until a surface deposit remains, which is only slightly acted upon by the corroding liquid. These facts are of the greatest importance and should always be borne in mind when considering the results of experimental tests, as they will frequently explain the startling differences between the results of actual practice and those obtained in experimental tests. Nearly all the results of experimental tests have been obtained by simple immersion of the alloy in water, dilute acid, or other corroding liquid; but in actual practice corrosion is usually accompanied by erosion to a greater or less extent, and the effect of this erosion in removing protective coatings and exposing fresh surfaces to the action of corrosion can readily be imagined, although it is often overlooked.

Another unavoidable drawback from which experimental tests suffer, is the fact that the results are always expressed in terms of loss of weight over a given surface. While this gives the relative corrodibility of different metals, it only takes into account the case of *uniform* corrosion and throws no light on the causes of trouble and breakdown occurring in actual practice. These troubles are almost invariably caused by local corrosion or pitting, and it is obvious that a certain loss of weight occurring locally may have more serious results than ten times that loss of weight distributed uniformly over the whole surface. Uniform corrosion is a more or less known factor, for which allowance can be made in design, but local corrosion is an unknown factor which defies calculation.

The greatest number of experiments on the subject of corrosion appear to have been carried out in connection with the corrosion of metals by sea water, and some of these may be briefly referred to. Milton and Larke, in an interesting paper on the "Decay of Metals," define "decay" as the solution of one constituent only of an alloy as distinguished from "corrosion" by which the metal is attacked as a whole. They confirm the statement that 1 per cent. of tin added to brass and Muntz metal assists them to resist corrosion or decay, and their conclusions are as follows:—

"1. Decay is more frequent in metals that have a duplex or more complex structure than in those which are comparatively homogeneous.

"2. Decay is due to slower or less energetic action than that causing corrosion; moreover, it requires an action which removes part only of the constituents of the metal, whereas 'corrosion' removes all the metal attacked.

"3. Both decay and corrosion may result from chemical action alone, or from chemical and electrolytic action combined.

"4. Pitting, or intense local corrosion, is probably often due to local segregation of impurities in the metal; but it may also in some places be due to favourable conditions furnished by local irregularities of surface or structure, producing local irregularities in the distribution of galvanic currents.

"5. For brass exposed to sea water, tin is distinctly preservative, while lead and iron are both injurious, rendering the alloy more readily corrodible. The percentage of the two latter metals, therefore, should be kept as low as possible in all brass intended for purposes where contact with sea water is inevitable.

"6. With a view to obtaining a minimum of corrosion the internal surfaces of condenser tubes should be as smooth and uniform as possible; and in order to ensure this condition, the cast pipe from which they are drawn should be smoothly bored inside, either before the drawing is commenced or in an early stage of the process, as is done in the manufacture of brass boiler tubes.

"7 The experiments with an applied electric current show that electrolytic action alone, even where exceedingly minute currents are employed, may result in severe corrosion or decay. Every effort, therefore, should be made to prevent such action by careful insulation of all electric cables. Where galvanic action is inevitable through the proximity of different metals exposed to the same electrolyte, the currents resulting should be neutralised by the application of zinc plates in the circuit, so arranged that they will be negative to both of the other metals."

Diegel has studied the same subject, and his results may be summarised as follows:—He finds that in brasses containing much zinc the addition of nickel exerts a beneficial influence. This is contrary to the experience of Mr Rhodin (whose work will be considered later), who states that "from a practical point of view nickel is incompatible with low percentage brasses."

The loss in weight in grams per square metre of several alloys suspended for twelve months in sea water is given by Diegel as

Mild steel	9·015
Copper-nickel (42 per cent. Ni) . . .	2·162
,, (20 per cent. Ni) . . .	1·848
Copper-aluminium (9 per cent. Al) . . .	0·600

In contact with iron the alloys suffered practically no loss.

Iron or zinc plates are almost invariably used for the protection of condenser tubes, and if these are of suitable composition and properly made troubles due to corrosion are reduced to a minimum. This is borne out by the statement of Mr Arnold Philip, the Admiralty chemist at Portsmouth, who says: "In spite of the fact that some millions of tubes are in use in the Royal Navy at any given moment, the number of cases coming under his notice in which localised corrosion has been observed do not at present amount at the most to more than about two per annum." He attributes the freedom from corrosion to three causes:—Firstly, to the composition of the alloy; secondly, to the satisfactory manner in which tube manufacturers are able to produce tubes of the exact composition specified; and, thirdly, to the consistent manner in which the use of steel, iron, or zinc protector slabs or bars has always been insisted upon.

As regards the copper-aluminium alloys, Carpenter and Edwards have compared five alloys of copper and aluminium with Muntz metal and naval brass. The alloys were suspended in sea water which was changed every week, and the results, expressed in change of weight in pounds per square foot per month, are shown in the following table:—

Alloy.	Composition.	Change in Weight.
2	1·06 per cent. Al.	·0028 lb.
4	2·99 ,, ,,	·0001
6	5·07 ,, ,,	·0000
9	7·35 ,, ,,	·0000
13	9·90 ,, ,,	+ ·0001
Muntz metal	...	– ·0014
Naval brass	...	·0018

The authors explain the gain in weight in the case of the alloy containing 9·9 cent. of aluminium by supposing that there is a slight oxidation of aluminium on the surface of the alloy.

A series of comparative tests carried out by immersion in sea water at Portsmouth Dockyard gave the following results:—

Alloy.	Composition.	Change in Weight.
2	1·06	0·0017
4	2·99	0·0009
6	5·07	0·0009
9	7·35	0·0009
13	9·90	0·0008
Muntz metal	...	0·0023
Naval brass	...	0·0012

In contact with iron and under the same conditions the alloys were completely protected, while the iron lost ·008 lb. per month. On the other hand, in fresh water and in contact with iron, the aluminium alloys were corroded, while the Muntz metal and naval brass suffered no loss. The actual results were as follows:—

Alloy.	Composition.	Change in Weight.
2	1·06 per cent. Al.	·0008
4	2·90 ,, ,,	·0008
6	5·07 ,, ,,	·0008
9	7·35 ,, ,,	·0010
13	9·90 ,, ,,	·0010
Muntz metal	...	·0000
Naval brass	...	·0000

In these experiments the aluminium alloys were from cast samples, while the Muntz metal and naval brass were from rolled samples, so that the results are not strictly comparable.

Manganese-bronze is practically unaffected by sea water, and is in consequence largely used in the manufacture of propellers and propeller blades. Rolled or malleable phosphor-bronze is also little affected by sea water, and has proved satisfactory where brass and steel were useless.

Apart from the corrosive action of sea water there are many important industrial problems connected with the corrosion of metals and alloys. There is a considerable demand, for example, for alloys suitable for the construction of pumps and pumping machinery dealing with corrosive liquids such as acid mine waters, and also for alloys suitable for evaporating pans, stirrers, etc., but, as already mentioned, there is very little reliable information connected with these subjects. The Bonifacius Coal Mining Company of Westphalia made a series of comparative experiments with wrought iron, steel, and delta metal, which showed very decided advantages in favour of delta metal. Bars 7½ inches long with a sectional area of ·62 inch were immersed in the mine water for 6½ months and the loss in weight determined. The results were as follows:—

	Wrought Iron.	Steel.	Delta Metal.
Weight of original bar .	1·1805	1·2125	1·2787
Weight of corroded bar .	·6393	·6614	1·2633

A series of experiments on the corrosion of copper alloys by acid mine water has also been described by a writer in the *Brass World.* In this case the water contained 12·58 per cent. of free sulphuric acid and 49·90 per cent. as sulphates. The six alloys tested had the following compositions:—

Alloy.	Copper.	Zinc.	Tin.	Lead.	Manganese.	Aluminium.	Iron.
Manganese-bronze, cast .	57·20	40·14	1·18	0·02	0·03	0·10	1·33
Manganese-bronze, rolled	62·45	36·00	0·63	0·06	0·02	...	0·84
Muntz metal, rolled .	57·55	40·02	1·49	0·56	...	...	0 38
Bronze	82·30	...	17·70	. .	...	...	...
Red brass . . .	80·75	1·73	8 73	8 74	...	. .	0·05
Hydraulic metal . .	83·05	6·00	10·81	0 10	...	...	...

The relative losses expressed in weight per cent. were—

Hydraulic metal	0·58	Bronze	2·00
Red brass	0·70	Manganese-bronze (rolled)	4·36
Muntz metal	1·83	Manganese-bronze (cast)	6·37

Unfortunately, in these experiments the samples were of different shapes, and it is obviously misleading to express the results in weight lost without considering the extent of surface subjected to corrosion. Evidently the results require confirmation.

With a view to determining the relative rates of corrosion of copper alloys in acid liquids the author carried out a series of tests on the following fourteen commercial copper alloys:—

1. Gun-metal.
2. Cast gun-metal.
3. Cast brass.
4. Rolled brass.
5. Cast phosphor-bronze A.
6. ,, ,, B.
7. ,, ,, C.
8. Cast phosphor-bronze D.
9. Manganese bronze.
10. Immadium bronze I.
11. ,, ,, II.
12. Aluminium-bronze.
13. Crotorite.
14. Rolled phosphor-bronze.

The liquids selected were sulphuric acid, sulphuric acid containing sulphate of iron, hydrochloric acid, and hydrochloric acid containing sodium chloride. The results, which are only comparative for the series, are given in grams dissolved per square metre of surface.

CORROSION IN A 10 PER CENT. SOLUTION OF SULPHURIC ACID.

1.	Immadium-bronze I	4·23
2.	Rolled phosphor-bronze	5·31
3.	Aluminium-bronze	7 00
4.	Cast phosphor-bronze C	7 37
5.	Rolled brass	7·43
6.	Cast brass	7·48
7.	Rolled gun-metal	7·52
8.	Cast gun-metal	8·13
9.	Cast phosphor-bronze B	8·54
10.	,, ,, D	10 56
11.	,, ,, A	11 36
12.	Crotorite	11·43
13.	Immadium-bronze II	12·02
14.	Manganese-bronze	13·83

CORROSION IN SULPHURIC ACID CONTAINING IRON SULPHATE.

1.	Immadium-bronze I	8·47
2.	,, ,, II	12·02
3.	Cast phosphor-bronze A	18·66
4.	Crotorite	21·96
5.	Rolled phosphor-bronze	22 51
6.	Rolled gun-metal	23·06
7.	Manganese-bronze	23·52
8.	Cast phosphor-bronze D	23·67
9.	Rolled brass	24·58
10.	Cast brass	24·80
11.	Cast gun-metal	24·91
12	Cast phosphor-bronze C	25·81
13	,, ,, B	27·13
14	Aluminium-bronze	29·76

Corrosion in a 20 per cent. Solution of Hydrochloric Acid.

1.	Immadium-bronze I	2·12
2.	,, ,, II	4·67
3.	Rolled brass	5·72
4.	Manganese-bronze	5·76
5.	Rolled phosphor-bronze	5·95
6	Aluminium-bronze	6·13
7.	Cast brass	6·69
8.	Crotorite	8·46
9.	Rolled gun-metal	8·72
10.	Cast phosphor-bronze A	9·13
11.	Cast gun-metal	9·40
12.	Cast phosphor-bronze B	9·61
13.	,, ,, C	11·47
14.	,, ,, D	16·48

Corrosion in a Solution of 20 per cent. Hydrochloric Acid and 10 per cent. of Sodium Chloride.

1.	Immadium-bronze II	28·94
2.	Rolled brass	31·45
3.	Manganese-bronze	32·75
4.	Immadium-bronze I	34·81
5.	Cast brass	35·63
6.	Aluminium-bronze	41·14
7.	Crotorite	44·83
8.	Cast phosphor-bronze A	45·44
9.	,, ,, B	46·56
10.	,, ,, C	47·11
11.	Rolled phosphor-bronze	48·54
12.	Rolled gun-metal	48·62
13.	Cast gun-metal	48·80
14.	Cast phosphor-bronze D	54·52

Mr Rhodin has made a special study of the corrosion of copper alloys, and he divides alloys into two classes which he describes as "balanced" and "unbalanced." Balanced alloys are supposed to be analogous to double salts, and the theory of solution is as follows:—When brass (to take an example) dissolves in hydrochloric acid, zinc chloride and copper chloride are formed. Now the heat of formation of zinc chloride is greater than that of copper chloride, hence in order that the total energy of the system may remain balanced, the "tendency to dissolve would vary directly as the heats of formation." Further, the zinc and copper will carry current in the direct ratio of their conductivities, and dividing by the densities, we have two expressions representing the ratio of the weights of each metal dissolved.

$$\frac{V \times M \times C}{D}$$

where V is the valency of the metal,
M the molecular heat of formation of the chloride,
C the conductivity,
and D the density.

In the case of brass, these expressions give values for copper and zinc of 61 and 39 respectively, which is approximately the composition of Muntz metal and the alloy which Mr Rhodin finds the least corrodible of the copper-zinc alloys In confirmation of this theory Mr Rhodin states that the addition of a more electropositive metal such as aluminium decreases the solubility of a brass containing 70 per cent. of copper, but increases that of brasses with less than 60 per cent. of copper; whereas the addition of an electronegative metal such as tin has exactly the reverse effect.

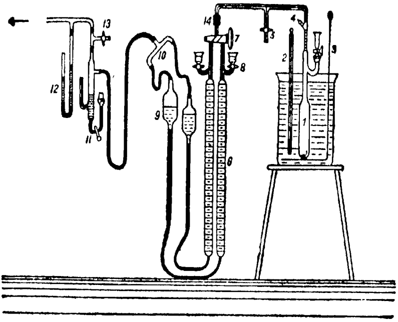

Fig. 51.—Rhodin's Corrosion Apparatus.

In order to compare the rates of dissolution of alloys Mr Rhodin has devised an apparatus for measuring the volume of hydrogen evolved during a given time. The apparatus is shown in fig. 51, and explains itself.[1] The water-bath in which the dissolution flask is immersed must be kept at exactly the same temperature, and two burettes are provided with a three-way cock, so that readings can be taken at intervals of ten minutes by using the burettes alternately. The alloy to be tested is drawn into wire about 0·5 mm. in diameter, and a length is cut off sufficient to provide a surface of 2 sq. cm. Strong hydrochloric acid is used as a solvent, and for copper alloys a temperature of 80° is maintained. Fig. 52 represents some curves given by Mr Rhodin as typical of the following alloys:—

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[1] Figs. 51 and 52 are inserted by permission of publishers of *Engineer*.

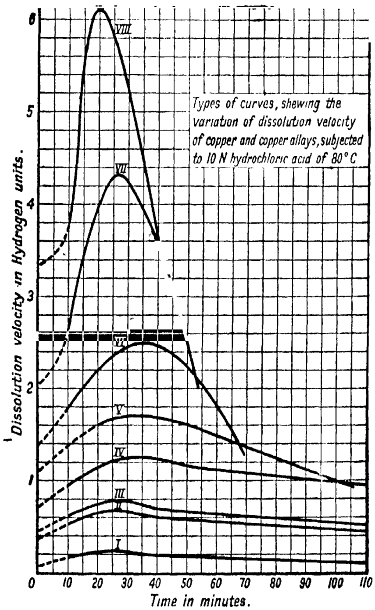

FIG. 52.—Rhodin's Typical Curves

I. Copper of good quality.
II. Bronze containing 90 per cent. copper and 10 per cent. Sn.
III. Admiralty gun-metal.
IV. Muntz metal and very good manganese-bronze.
V. Brass containing 70 per cent of copper.
VI. Low percentage brasses, rich in iron.
VII. and VIII. Low percentage brasses of manganese-bronze type which contain incompatible ingredients.

As the result of his experiments Mr Rhodin arrives at the conclusion that in a given series of copper alloys "the alloy which has the flattest and most regular dissolution curve does at the same time possess the best mechanical properties."

A great many papers have been written on the subject of the corrosion of non-ferrous metals and alloys to which it is unnecessary to refer in detail here. An excellent summary of these papers has been given by Bengough in a report to the Corrosion Committee of the Institute of Metals published in 1911.

As regards the corrosion of steel and iron alloys Howe has made a number of exhaustive trials with wrought iron, steel and nickel steel. The plates tested in these experiments weighed 2597 lbs., and the total area exposed was 928 sq. ft. The results are summed up in the following table, wrought iron being taken as the standard in each case:—

	Sea Water.	Fresh Water.	Atmosphere	Average.
Wrought iron . .	100	100	100	100
Mild steel . . .	114	94	103	103
3 per cent. nickel steel .	83	80	67	77
26 per cent. nickel steel .	32	32	30	31

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CHAPTER VII.

COPPER ALLOYS, BRONZE.

It is customary to consider the alloys of copper under three heads, viz. (1) The bronzes, or alloys consisting mainly of copper and tin; (2) the brasses, consisting mainly of copper and zinc; and (3) other alloys of copper. Although not an entirely satisfactory classification, there is much to be said in its favour, and it is to be regretted that manufacturers in some instances use the terms brass and bronze indiscriminately. Alloys, for example, containing from 60 to 70 per cent. of copper and 30 to 40 per cent. of zinc, together with small percentages of iron, aluminium, or manganese, would be far more accurately described as brasses than bronzes, and yet these alloys are frequently described and sold as bronzes. If such alloys contain aluminium or manganese, or even if these metals have been employed in their manufacture, they might be described as aluminium-brasses or manganese-brasses, but not bronzes. The terms brass and bronze are so firmly established in the English language that it would be impossible (even if desirable) to adopt any other classification, and the words should therefore be employed with discretion.

Bronze.

Historical.—The word *bronze*, derived from the Italian *bronzo*, appears to have been introduced into the English language in the 16th century. The alloy, however, was known in very early times, and a rod of metal found by Dr Flinders Petrie at Meydum, and estimated to belong to a period about 3700 B.C., was found to contain 89·8 per cent. of copper and 9·1 per cent. of tin, together with small quantities of impurities. Whether the tin is present as an impurity or whether it was added intentionally it would be difficult to say; but it is curious that the proportion of tin to copper is very nearly the same as that of modern bronze.

Some battle-axes and other objects from the deposits, which Schliemann dated at about 1200 B.C., and which he identified with Troy, were found to consist of copper and tin, the tin varying from 3·8 to 8·6 per cent.; whereas the objects found in the earlier deposits were of copper. The oldest relic which can be dated with any accuracy is a sceptre of Pepi I. (6th dynasty), which is almost pure copper. All the available evidence seems to prove that a copper age preceded the bronze age, and it is more than probable that the production of bronze was in the first place the result of accident, and that the intentional addition of tin to copper was only the result of experience. Bronzes have been found in Egypt dating from very early times. In Greece bronzes were very rare in Homeric times (900 B.C.), and the Greek and Trojan heroes (1194–1184) used copper for their armour, swords, knives, and spear-heads.

As regards the relation of the bronze age to the iron age there has been much controversy, and it has been proved by recent discoveries that the iron age is of a much earlier date than was formerly supposed. At Hallstadt, in Upper Austria, no less than 6084 objects were obtained from a prehistoric cemetery. These include tools of copper and bronze and swords both of copper and iron, together with those of a transition period having blades of iron and handles of copper. Montelius considers that the bronze swords belong to a period about 850 to 600 B.C., and the iron swords to a period about 600 to 400 B.C.

In Egypt, Assyria, and Babylonia instruments of bronze have also been found, together with those of iron; while in Ireland, India, Cyprus, and other countries, weapons of almost pure copper and similar in form to those of stone have been found; so that it appears safe to conclude that the bronze age overlapped on the one hand the age of copper, and possibly the age of stone; and, on the other hand, the great age of iron. The earliest bronzes consist almost entirely of copper and tin; but many of the Roman bronzes contain large quantities of lead. The addition of lead is, in fact, due to the Romans, and first appears in *aes* *signatum* (429–451 B.C.). The following table gives the analyses of some ancient bronzes:—

	Copper.	Tin.	Lead.	Iron.
Celtic vessels	88·0	12·0	...	...
Bronze nails	95·1	4·9	...	...
Bronze (Troy, 1200 B.C.)	90·7	8·6	...	...
Bronze ,, ,,	93·8	5·7	...	...
Roman sword blade	91·4	8·4	...	...
Coin of Ptolemy IX.	84·2	15·6	...	...
Athenian coin	89·4	9·9	...	...
Coin of Alexander the Great	86·7	13·2	...	...
Axe-head	88·0	11·2	0·8	
Attic coin	88·5	10·0	1·1	...
Coin of Julius Cæsar	79·1	8·0	12·8	...
Roman As. (B.C. 500)	69·7	7·2	21·8	0·5
Sword blade	89·5	10·0		0·4
Egyptian statue	81·2	2·5	16·0	...
,, statuette Osiris (300–200 B.C.)	76·8	11·2	11·7	
Greek statue, fifth century B.C.	84·5	9·5	5·3	...
,, ,, fourth ,, ,,	89·0	6·1	4·9	...
,, vase ,, ,, ,,	81·7	10·9	5·3	0·1
Roman statue	78·3	10·8	10·2	0·1
,, statuette	78·8	9·0	12·1	0·1

The presence of lead in bronze was probably due, in the first place, to the fact that the tin was adulterated with that metal; but it was probably soon discovered that the addition of lead conferred valuable properties upon the alloy, and the bronzes of later date almost invariably contain appreciable amounts of lead.

The presence of zinc in bronze was also probably the result of accident, due to the introduction of zinc ore into the furnace charge. An Etruscan bronze, dated the fifth century B.C., was found to contain 0·73 per cent. of zinc. Early Japanese bronzes have also been found to contain appreciable quantities of zinc as well as lead.

Modern Research.—The most convenient date from which to begin the study of modern research on the copper-tin alloys is 1879, for in that year the Committee on Alloys appointed by the United States Board published a table in which the results of their own researches and those of previous workers were collected. This table has been frequently quoted in books dealing with alloys, and as it contains much valuable information in a condensed form it is inserted here:—

PROPERTIES OF COPPER TIN ALLOYS.

No.	Atomic Formula.	Composition of Original Mixture		Composition by Analysis		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility. (Mallet.)	Relative Ductility (Thurston)	Hardness (Mallet, Calvert, Johnson)	Order of Malleability (Mallet.)	Order of Fusibility (Mallet.)	Conductivity for Heat. Silver = 100	Conductivity for Electricity. Silver = 100	Authority	Remarks.
		Cu.	Sn	Cu.	Sn													
1	..	100	0	..	..	8 791*a* 8·874*b*	Copper-red	Fibrous	27,800	..	30 08	.	..	..	..	..	U S B	*a* Specific gravity of bar *b* Specific gravity of turnings from ingot
2	..	100	0	..	..	8 667	Tile-red	Earthy	55,104	1	.	10	2	16	.		Ml	
3	..	100	0	..	..	8 921	..	..	.	..	.		..	.		93 16	Ma	
4	..	100	0	..	..		..	..	..	..	.	301	..	..	81 1	..	C. J	
5	..	100	0	..	..	8·794	..	..	..	..	..	.	..	..		..	Cr.	
6	..	100	0	..	..	8 921	..	..	..	..	..	..	..	..		..	Mar.	Cast copper
7	..	100	0	..	..	8 952	..	..	.	..	..	..	..	..		..	Mar.	Sheet copper
8	..	100	0	..	..		..	..		..	..	.	..	..	73·6	79·3	We.	
9	..	100	0	..	..	8·672	..	..	24 252	..		.	..	..	..	.	Wa	Mean of nine samples.
10		98·59	1·41	.	.		..	.	..	.	100 1	.	..	..	..	62·46	Ma	
11	$SnCu_{96}$	98 1	1·9	97·89	2 11	8 564	Red	Vesicular	..	..		..	..	..	..	..	U.S B	Defective bar.
12		98 04	1 96	..	..	..	..	..	..	..	.	..	..	..	..	..	Bo	Can be forged like copper.
13	..	98	2	..	..	..	..	..	..	..	..	..	..	..	..	..	La.	Ramrods for guns
14	..	97 5	2 5	..	..	8 511	Red.	Vesicular	..	..	.	..	..	..	..	..	U.S.B	Defective bar
15	..	96 97	3 03	..	..	.	..	.	.	..	.	.	..	..	..	..	W.	Resists action of hydrochloric acid.
16	$SnCu_{48}$	96·27	3·73	96 06	3·76	8 649	Reddish-yellow.	Vesicular.	32,000	..	70 3	.	..	..	..	..	U.S B	
17	..	96	4	..	..	8 947	..	..	..	..	..	..	..	..	..	..	Rl.	Annealed and compressed.

18	..	95	5	..	..	..	Golden-yellow.	..	..		..	..	..	..	..	..	W.	Hard, malleable.
19	..	94·1	5·9	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Pieces of machines
20	..	94	6	..	..	8 939	..	..	..	..	..	..	..	..	..	..	Ri.	Specific gravity after repeated tempering.
21	..	93·98	6·02	..	..	..	..	..	..	..	.	..	..	..	.	19 68	Ma.	
22	$SnCu_{25}$	93·17	6·83	..	..	8·82	..	..	..	..	..	602 8	..	..	..	..	C J.	
23	$SnCu_{24}$	92·8	7 2	..	..	8 694	Reddish-yellow	Vesicular.	28,540	..	21 9	..	..	..	..	..	U.S.B.	
24	..	92·5	7·5	..	..	8·684	,,	..	27,900	..	43·2	..	..	..	..	..	U S B.	
25	..	92	8	..	..	..	..	..	..	.	..	..	..	..	..	..	Bo	Bronze for medals
26	..	91 75	8·25	..	..	..	..	..	..	...	..	..	..	..	..	..	W.	Shows separation of metals when examined with a lens.
27	..	91·74	8·26	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	English ordnance
28	..	91 7	8 3	.	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Ordnance metal
29	.	91 66	8·33	..	..	.	..	..	..	..	..	.	..	..	..		Bo	Eight - pounder guns.
30	$SnCu_{20}$	91·9	8·1	..	..	8 793	..	..	..	..	..	63 958	..	..	..	..	C. J	
31	..	91·3	8 7	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Toothed wheels.
32	..	90·91	9·09	..	.	.	..	..	32,093	..	.	..	..	..	..	..	Mus	Prussian ordnance.
33	..	90·9	9 1	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Ordnance metal
34	..	90·73	9 27	..	..	..	..	.	..	.	..	..	..	..	..	..	Bo	French ordnance
35	..	90 1	9·9	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	
36	..	90	10	90·27	9·58	8·669	Greyish-yellow.	Earthy.	26,860	.	18	..	..	..	..	..	U.S B.	Compressed ordnance bronze.
37	..	90	10	..	..	8 875	..	..	..	..	..	..	..	..	..	..	De.	After repeated compression.
38	..	90	10	..		8·935	..	..	..	..	..	..	..	..	..	..	Ri.	Railway - car bearings.
39	..	90	10	..	..	..	..	..	..	.	..	..	..	..	..	..	Bo.	Ordnance metal
40	..	89·3	10·7	..	..	..	..	..		..	..	..	..	..	..	..	Bo	Small bar cast in iron mould
41	..	89 29	10·71		..	8 953	..	..	37,688	..	..	..	..	..	..	..	Wa.	Small bar cast in clay mould.
42	..	89·29	10·71	..	..	8·313	..	..	25,783	..	..	..	..	..	..	..	Wa.	Mean of twelve gun-heads.
43	..	89·29	10·71	..	..	8 353	..	..	26,011	..	..	..	..	..	..	..	Wa.	Ordnance metal.

PROPERTIES OF COPPER-TIN ALLOYS—*continued*.

No.	Atomic Formula.	Composition of Original Mixture.		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility (Mallet.)	Relative Ductility. (Thurston.)	Hardness. (Mallet, Calvert, Johnson.)	Order of Malleability. (Mallet.)	Order of Fusibility. (Mallet.)	Conductivity for Heat Silver=100.	Conductivity for Electricity. Silver=100	Authority.	Remarks.
		Cu.	Sn.	Cu.	Sn.													
44	..	89·23	10·77	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Mean of eighty-three gun-heads.
45	$SnCu_{15}$	89	11	..	..	8·84	..	..	..	..	..	..	..	..	..	..	Ri.	
46	$SnCu_{15}$	88·97	11·03	..	..	8·825	..	..	..	..	..	77292	..	..	..	..	C. J	
47	..	88·89	11·11	..	..	8 523	..	..	..	..	..	..	..	..	..	..	Wa.	Gun-metal.
48	..	88·39	11·61	..	..	..	..	..	..	..	..	..	..	..	..	12 1	Ma.	
49	..	88	12	..	..	.	..	..	..	..	..	..	..	..	..	..	La.	
50	..	87·65	12 35	..	..	..	..	..	..	..	.	..	..	..		10 15	Ma.	
51	..	87·5	12·5	..	..	8 648	Greyish-yellow.	Earthy.	31,100	..	7 3	..	..	..	..	..	U.S.B	
52	..	86·8	13·2	..	..	..	..	..	.	..	..	..	..	..	..	..	W.	*a*. Specific gravity of bar.
53	$SnCu_{12}$	86 57	13·43	87·15	12·73	8·681*a*	Mottled.	Finely vesicular.	29,430	..	13 09	..	..	..	..	..	U.S.B.	*b* Specific gravity of fine turnings.
						8·943*b*	White and yellow.											
54	..	86·21	13 79	..	..	8·87	..	..	..	..	..	..	..	..	..	..	W.	Densest of all alloys? (Riche).
55	..	86	14	..	..	..	..	..	..	..	..	..	..	..	..	..	W.	Axle-tree bed Seraing locomotive.
56	..	85·71	14·29	..	..	..	..	..	44,071	..	..	..	..	..	..	..	Mus.	
57	..	85·09	14 91	..	..	..	..	..	..	..	..	..	..	..	..	8·82	Ma.	
58	$SnCu_{10}$	84 33	15 67	..	..	8·87	..	..	.	..	..		..	..	..	..	Ri.	
59	..	84·32	15·68	..	..	8·832	..	..	..	..	..	..	916·66		..	..	C. J	
60	..	84·29	15 71	..	..	8·561	Reddish-yellow	Finely crystalline.	36,064	2	..	8	6	15	..	..	Ml.	
61	..	84	16	..	..	..	..	.	..	..	..	..	..		..	..	Bo.	Carriage-wheel boxes.

62	..	83·3	16·7	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Jeweller's punches.
63	$SnCu_9$	82·81	17·19	..	..	8·462	Reddish-yellow.	Finely crystalline	34,048	3	..	5	7	14	..	..	Ml.	
64	..	82·5	17·5	..	..	8·792	Reddish-grey.	,,	36,200	..	0·82	..	..	..	..	..	U.S.B	Strongest of series
65	..	82	18	..	..	8·927	.	..	..	..	..	..	..	..	..	..	R	Annealed and tempered.
66	$SnCu_8$	81·15	18·85	..	..	8·86		..	..	.	..	..	..	..	..	..	Ri	
67	$SnCu_8$	81·1	18·9	..	..	8·459	Yellowish-red.	Finely crystalline	39,648	4	..	4	10	13	..	..	Ml	
68	..	..	..	80·43	19·57	8·953	..	..	..	..	..	..	..	..	..	..	Th	Chinese gong
69	..	80	20	..	..	8·7	..	..	..	..	..	..	..	..	..	..	Bo	Bells of Reichenhall, 300 years old
70	..	80	20	..	..	..	..	..	35,739	..	..	..	..	..	..	..	Mus	
71	..	80	20	..	..	8·85	..	.	..	..	..	..	.	..	..	..	Ri	Annealed and tempered
72	..	80	20	..	..	8·955	..		..	..	..	..	..	..	..	..	Ri	After repeated compression.
73	..	80	20	80·95	18·84	8·74	Reddish-grey.	Finely granular.	32,980	..	0·4	..	..	..	..	..	U.S.B	
74		79·2	20·8	..	.	8·927	..	..	..	..	..	..	..	..	..	..	Ri	Annealed and tempered
75	$SnCu_7$	79·02	20·98	..	.	8·90	..	..		..	..	.	..	..	..	..	Ri	
76	$SnCu_7$	78·97	21·03	.	.	8·728	Yellowish-red	Vitreous conchoidal	30,464	5	..	3	11	12	.	..	Ml	
77	..	78	22	..		.			.	..		.	.	..	.		Bo	
78	..	77·5	22·5	..	.	8·917	Pinkish-grey.	Finely granular.	24,650	..	0·03	..	..	..		..	U.S.B	
79	$SnCu_6$	76·32	23·68	76·64	23·24	8·565		Smooth	22,010	.	0·02	..		.	..	.	U.S.B	
80	$SnCu_6$	76·31	23·69	..	..	8·91										.	Ri	
81	$SnCu_6$	76·29	23·71	..	..	8·75	Bluish-red	Vitreous	21,728	0	..	2	12	11		..	Ml.	
82	.	76·2	23·8	..	..	9·1 (?)	..	.		..	..		.			.	Bo	Church bell in Reichenhall 600 years old
83	.	75·2	24·8	..	..	..	..	.			..				..	..	Bo	Swiss clock bells brittle
84	..	75	25	..	..		.	..	.	.	..		..		.	.	W	
85	$SnCu_5$	72·91	27·09	..	..	8·87	Reddish-white.	..			.	..	.	.	.	..	Ri	

PROPERTIES OF COPPER-TIN ALLOYS—*continued*.

No.	Atomic Formula	Composition of Original Mixture		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs per square inch.	Order of Ductility (Mallet)	Relative Ductility (Thurston)	Hardness. (Mallet, Calvert, Johnson)	Order of Malleability. (Mallet)	Order of Fusibility. (Mallet)	Conductivity for Heat Silver=100.	Conductivity for Electricity. Silver=100	Authority	Remarks.
		Cu	Sn.	Cu	Sn.													
86	$SnCu_5$	72·9	27·1	..		8·965						Broke			20·7	..	C. J.	
87	$SnCu_5$	72·8	27·2	..		8·575	Bluish-red	Conchoidal	10,976	0		1	13	10			Ml	
88	..	72·5	27·5	.	.	8·925	Reddish-white	„	6,493		·003			.		.	U S B	
89	..	70	30	69·94	29·89	8·932	White	„	5,585		·008	.		.			U S B	
90	..	68·82	31·18	.	.			..			..		.		.		Bo	Mirror of telescope
91	$SnCu_4$	68·28	31·72	..		8·80	..	..		.	.					.	Ri	
92	$SnCu_4$	68·27	31·73	..		8·948						Broke				..	C J	
93	$SnCu_4$	68·25	31·75	68·58	31·28	8·938	White	Conchoidal.	1,620						15·5	..	U S B	
94	$SnCu_4$	68·21	31·79	.		8·40	Ash-grey		1,568	0		6	14	9		..	Ml	
95	..	68·21	31·79	.	.								.			..	Bo	Mirror metal
96	..	67·5	32·5	.	.	8·907	White Steel grey	Conchoidal.	2,536		·009		.		..	..	U S B	
97	..	66·67	33·33	..	.							..	..		..	..	W	Hard, uniform
98	..	66·67	33·33	.	.			..	1,017			.		.		..	Mus	
99	..	65	35	65·34	34·47	8·947	Bluish-grey	.	2,201		·002	.	.	..	.	..	U S B.	
100	..	62·5	37·5	.	.	8·956	Dark grey	Radiated crystalline	1,561		·001	.			..	..	U.S.B.	
101	$SnCu_3$	61·79	38·21	..	..	8·954	.		..			Broke		.	49·4		C J	
102	$SnCu_3$	61·79	38·21	..	..	8·96	.		.						.	..	Ri	
103	$SnCu_3$	61·71	38·29	..	..	8·97	Dark grey.	Rough, stony	688		·003				..	..	U S.B	Greatest density, weakest
104	$SnCu_3$	61·69	38·31	..	..	8·539	„	Tabular crystalline	1,120	0	..	7	16	8	..	..	Ml	
105	..	60	40	..	..	..	..	.	..	..	..	..	.	..	..	..	Bo.	White bell-metal.

106	..	57·5	42·5	..	..	8·781	Light grey.	Stony	1,377		·001	..	..	..	..	..	U.S.B.	
107	Sn_5Cu_{12}	56·32	43·68	56·7	43·17	8·682	,,	,,	1,455		·003	..	..	..	..	..	U.S.B.	
108	.	52·5	47·5	..	.	8·643	,,	,,	..	..	·001	..	..	..	.	..	U.S.B.	Weakest under transverse stress
109	$SnCu_2$	51·84	48·16	.	.	8·57	..	..	..	..	.		..	..	..	..	Ri	
110	$SnCu_2$			..	.	8·512		..	.	..	.			.	.	.	Cr	
111	$SnCu_2$	51·83	48·17	.		8·533	..	..			..	Broke		..	42·8	..	C J	
112	$SnCu_2$	51·8	48·2	51·62	48·09	8·56	Light grey.	..	2,555	.	·003						U S B	Remarkable for liquation
113	$SnCu_2$	51·75	48·25	..		8·416	Grey white.	Vitreous conchoidal	3,808	0	..	9	15	7	.	..	Ml	
114	..	50	50	.	..	..		.	725	..	..	..			..	.	Mus	
115	..	50	50			8·79	Bluish white	.	.	..	..	.			..	.	W	Very slightly malleable.
116	Sn_7Cu_2	47·95	52·05	47·61	52·14	8·442	Greyish white	Fine grain.	1,525	.	·003		.	.	..		U S B	
117	.	47·5	52·5		.	8·446	,,	Crystalline.	2,407	.	·003	..	..				U S B	
118	Sn_2Cu_3	44·67	55·33	.		8·3	,,	.		.			..		.		Ri	
119	Sn_3Cu_3	44·63	55·37	44·52	55·28	8·312	,,	Crystalline	3,010		·003				..		U S B	
120	..	42·5	57·5		.	8·437	,,	..	2,098		·006		.	.	..	.	U S B	
121	Sn_3Cu_4	41·74	58·26	42·38	57·30	8·302	,,	..	3,910	.	·007			.	..	..	U S B.	
122		40	60				,,						.	.	..	.	Le	White bell-metal
123	Sn_5Cu_6	39·2	60·8	38·37	1· 3	8·182	Greyish white.	Crystalline.	2,820	.	·005	.		..	..	.	U S B	
124		37·5	62·5	.	..	8·101	,,	,,	2,400	..	·004	.		.	.		U S B	
125	SnCu	34·99	65·01	.	..	8·12		,,	..	..	.			.		.	Ri	
126	SnCu	34·98	65·02	.	..	7·992		,,		.		Broke		..	41·5	.	C J.	
127	SnCu	.	.		.	8·072				.						.	Cr	
128	SnCu	34·95	65·05	34·20	65·8	8·013	Greyish white	Crystalline	3,371	..	·005				.		U S B	
129	SnCu	34·92	65·08	..	..	8·056	,,	Tabular crystalline	3,136	0		11	9	6	..	..	Ml	
130	..	33·33	66·67	.	..		White							..	..	.	W	Brittle, uniform
131	..	32·5	67·5	..	..	7·931	Greyish white	Crystalline.	2,322	.	·014			..		.	U S B	
132	Sn_4Cu_3	28·72	71·28	25·85	74	7·918	,,	,,	1,648		·011		.	.	..	..	T	
133	.	27·5	72·5	.		7·915	,,	,,	4,380		·018		..	.	..	.	T	
134	.	25	75	.		7·813	Bluish white	,,	..		.	.	.	.		..	W	
135	Sn_5Cu_3	24·38	75·62	23·35	76·29	7·835	Greyish white	Finely crystalline	6,775	.	·03				..	..	T.	
136		22·5	77·5	.	.	7·774	,,	,,	5,000	..	12	..		.	.	.	T	
137	..	21·74	78·26	22·36	77·63	7·53	Whitish.	.	..	..	.	..			.	.	W	Yellow, greenish white

PROPERTIES OF COPPER-TIN ALLOYS—*continued*

No.	Atomic Formula	Composition of Original Mixture		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility. (Mallet.)	Relative Ductility. (Thurston.)	Hardness. (Mallet, Calvert, Johnson.)	Order of Malleability. (Mallet.)	Order of Fusibility (Mallet.)	Conductivity for Heat Silver=100.	Conductivity for Electricity. Silver=100	Authority	Remarks.
		Cu	Sn.	Cu	Sn													
138	Sn_2Cu	21·21	78 79	..	.	7·738	..	..	..	..	..	135 42	..		43·1	..	C J.	
139	Sn_2Cu	21·21	78 79	..	.	7·74			..		..	.	..	..	..	..	Ri.	
140	Sn_2Cu	21·18	78·82	20 25	79·63	7 77	Greyish white.	Crystalline.	4,337	.	·06		.	..	..	..	T.	
141	Sn_2Cu	21·15	78 85	..	..	7 387	,,	,,	8,736	0	..	12	8	5	..	..	Ml	
142	Sn_5Cu_2	17·68	82 32	..	..	7·652				.	..	.	..		..	..	Cr	
143	..	17 5	82 5	..	..	7·69	Greyish white.	Crystalline.	2,816		·2	..	.		.		T	
144	.	16·4	83 6	..	..		.	.	..	..		..	..	..	.	12 76	Ma.	
145	Sn_3Cu	15·21	84 79	.	..	7 53			..	.			.	..	.	.	Ri	
146	Sn_3Cu	15·21	84 79	.	.	7 606				.	..	104 17	.	..	42·3	.	C J.	
147	Sn_3Cu	15 19	84 81	15·08	84·62	7·657	Greyish white.	Crystalline.	6.520		·92	.	.	.	.	..	T.	
148	Sn_3Cu	15·17	84 83	..		7 447	,,	Coarsely crystalline	6,944	0	.	13	15	4	..	..	Ml	
149	..	12 5	87 5	..		7·543	,,	Crystalline	3 798		4 71	.	..	..	..	..	T.	
150	Sn_4Cu	11 86	88 14	..	.	7 558	..			..	.	95 81	..	.	40·6	..	C. J.	
151	Sn_4Cu	11 84	88 16	11·49	88 47	7·552	Greyish white.	Crystalline	6,380	..	7 08	.	..	..	.	..	T	
152	Sn_4Cu	11·84	88 16	..	..	7 5		..		.	..	..		..	.	..	Ri.	
153	Sn_4Cu	11 82	88 18	..	.	7 472	Greyish white.	Coarsely crystalline.	6,944	8	.	14	4	3	.	..	Ml.	
154	Sn_5Cu	9·73	90 27	..	..	7·517	..	..	.	..	.	83 33	..	..	39 6	..	C. J.	
155	Sn_5Cu	9·73	90 27	..	..	7·52	.	..	..	..		..	..	..	..	..	Ri.	
156	Sn_5Cu	9·7	90 3	8·57	91·39	7·49	Greyish white.	Granular.	6.450	..	23·47	..	..	..	..	..	T.	
157	Sn_5Cu	9·68	90·32	..	..	7 442	,,	Earthy.	3,360	6	..	15	3	2	..	..	Ml.	

158	..	9·09	90·91	..	..	7·472	..	..	..	..	..	..	..	..	..	..	W.	Slightly malleable.
159	..	7·5	92·5	..	..	7·417	Greyish white.	Granular.	6,096	..	40·06	..	..	..	..	..	U.S.B.	
160	..	6 43	93 57	..	..	..	..	..	..	..	..	..	..	..	..	12 03	Ma.	
161	$Sn_{12}Cu$	4·29	95·71	3·72	96·26	7·36	Greyish white.	Granular.	4,780	..	56·77	..	..	..	..	.	U.S.B.	
162	..	2·5	97·5	..	..	7 342	,,	Fibrous	5,600	..	121·9	..	..	..	..	.	U S B.	
163	$Sn_{48}Cu$	1·11	98·89	·74	99·02	7·305	,,	,,	3,650	..	133 9	..	..	..	..	..	U S B.	
164	$Sn_{96}Cu$	·56	99·44	·32	99 45	7·299	,,	,,	4,475	..	208 8	..	..	..	..	..	U S B.	
165	Sn	0	100	..	..	7·293	,,	,,	3 500	..	219 8	..	..	..	..	..	U S B.	
166	..	0	100	..	..	7·291	White.	,,	6,040	7	.	16	1	1	..	..	Ml.	
167	..	0	100	..	..	7·297	.	..	2,122	..	..	..	..	..		.	Wa.	
168	..	0	100	..	..	7·294	..	..	.	..	..	..	..	..		11·45	Ma.	
169	..	0	100	..	..	7·305	..	..	..	..	..	..	..	..	.		Cr	
170	..	0	100	..	..	.	..	..	..	..	..	27	..	..	42·2		C J.	
171	.	0	100	..	..	..	..	..	..	..	..	..	..	..	15·2	17	We.	

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T Thomas Thomson, *Annales de Chimie*, 1814, vol lxxxix pp 46-58
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Wa.-Major Wade, United States Army, *Report on Experiments on Metal for Cannon*, Phil, 1856
We.--Weidemann, *Phil Mag*, 1860, vol xix pp. 243, 244.

In the foregoing table the figures of order of ductility hardness, and fusibility are taken from Mallet's experiment on a series of sixteen alloys, the figure 1 representing th maximum and 16 the minimum of the property. The ductilit of the brittle metals is represented as 0. The relative ductilit given in the table of the alloys experimented on by the U S Board is the proportionate extension of the exterior fibres of th pieces tested by torsion, as determined by the autograph strai diagrams It will be seen that the order of ductility differ widely from that given by Mallet.

The figures of relative hardness, on the authority of Calver and Johnson, are those obtained by them by means of a indenting tool. The figures are on a scale in which cast iro is rated at 1000. The word "broke" in this column indicate that the alloy opposite which it occurs broke under the indentin tool, showing that the relative hardness could not be measured but was considerably greater than that of cast iron.

Since the publication of this table the copper-tin alloys have bee subjected to a very thorough investigation, and their physical an chemical as well as their mechanical properties have been studied It would take too long to consider the various researches in detail but the results may be briefly stated. The melting-points an the microscopical examination of the alloys have already bee referred to, and in addition to these Laurie (and more recentl

Herschkowitsch) have determined the electromotive force, Lodge has determined the conductivity and Herschkowitsch has determined the heat of formation. It has also been shown by Ledoux that the thermo-electric power has a maximum value for the composition corresponding to Cu_3Sn and a minimum for the composition corresponding to Cu_4Sn

The variations in the physical properties of the series are plotted in fig. 14, and it will be observed that the evidence in support of the existence of a definite compound corresponding to the formula Cu_3Sn is overwhelming

A glance at the curves representing the physical and mechanical properties of the copper-tin alloys (figs 14 and 15) will show that from a mechanical point of view the middle members of the series are valueless, and in fact the useful alloys do not contain more than 25 per cent. of copper These in turn may be divided into two classes, viz · (1) gun metal, containing from 8 to 14 per cent. of tin ; and (2) bell-metal, containing from 15 to 25 per cent of tin.

Gun-metal, as is well known, derives its name from the fact that before the introduction of steel as a material for the manufacture of guns they were made of this alloy

The following table, giving the composition of the actual alloys employed in the manufacture of ordnance by the different countries, shows that, with the exception of the Chinese, there is not much difference between them

	Copper	Tin.	Iron	Zinc	Lead
English ordnance .	91·74	8·26	...	...	...
8 pounder guns .	91·66	8·33	...	...	...
Prussian ordnance .	90·91	9·09	...	...	...
French „ .	90·73	9·27	...	...	...
American „ .	90·00	10·00	...	...	...
Russian „	88·61	10·70	·69	...	...
Swiss „	88·93	10·38	·11	·42	·06
Chinese „	77·18	3·12	1·16	5·02	13·22
„ „	93·19	5·43	1·38	...	...

The bronzes containing from 8 to 11 per cent. of tin are the most suitable where a combination of strength, elasticity, toughness, and ability to withstand shock are required The alloy containing 9 per cent. of tin has a tensile strength of about 16 tons per square inch, with an elastic limit of 6·5 tons per square inch and an elongation of 16 per cent.

Gun-metal, as has already been stated, consists of a solid solution of tin in copper containing a certain amount of the definite compound Cu_4Sn. When viewed under the microscope the solid solution is yellow in colour, while the compound is almost white. It is curious that this constituent does not form until the alloy is completely solid; and moreover, as was first pointed out by Charpy, it never occurs in a uniform mass, but is always more or less broken up. Photographs 9 and 10 show the appearance of a gun-metal magnified 100 diameters, and photograph 11 shows the appearance of the Cu_4Sn under a higher magnification.

Influence of Heat Treatment on Bronzes.—It has already been shown that the bronzes containing from 9 to 22 per cent. of tin pass through three distinct stages during solidification. In the first place, a solid solution of tin in copper (Heycock and Neville's α constituent) separates out at temperatures varying from 1020° in the case of the bronze containing 9 per cent. of tin to 860° in the bronze containing 22 per cent. of tin. At 790° the remainder of the alloy solidifies in the form of a second solid solution (Heycock and Neville's β constituent) containing from 22·5 to 27 per cent. of tin. The solid alloy now consists of two solid solutions and undergoes no further change until the temperature falls to 500°, when the β solution is no longer stable but breaks up with the formation of the δ constituent, which is probably the compound Cu_4Sn. The alloy now consists of a mixture of α and δ, and is stable at the ordinary temperature.

It is obvious from the foregoing considerations that heat treatment must have a very decided influence on the physical properties of the alloy. If, for example, the bronze is quenched at a temperature above 500° the formation of Cu_4Sn (a hard, brittle constituent) is prevented, and the alloy is more malleable and stronger. The change is most strongly marked in the case of the alloys rich in tin.

Guillet has made some experiments on the mechanical properties of bronzes quenched at various temperatures, and his results confirm the conclusions which would be drawn from theoretical considerations. The curves in fig. 53 are plotted from Guillet's

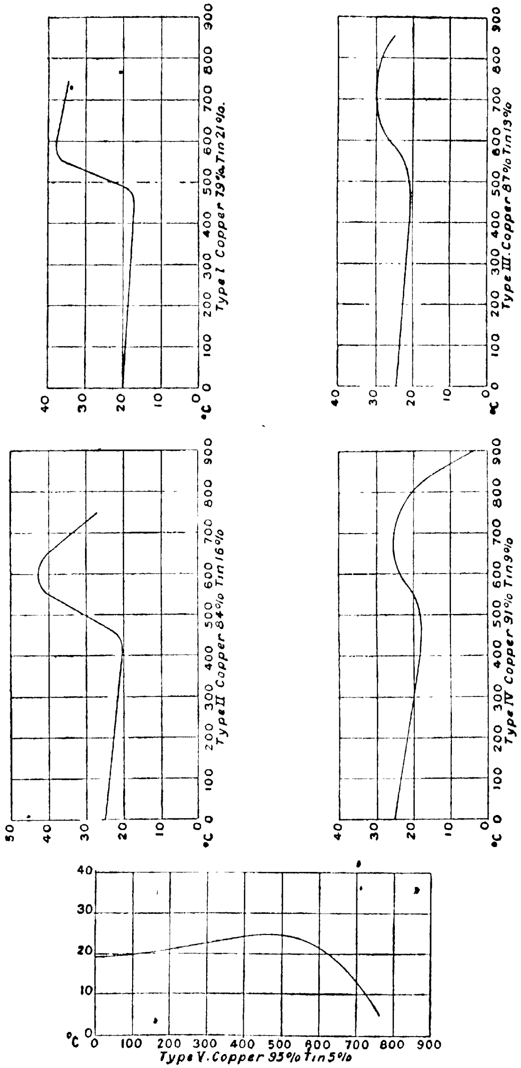

FIG. 53.—Tensile Strength of Quickly-cooled Bronzes

figures, and represent the breaking strain of five bronzes containing respectively 95, 91, 87, 84, and 79 per cent. of copper. These results explain the fact, which has long been known, that bronze can be forged at a temperature just below redness, and that bronzes quenched at or above that temperature become malleable. The Chinese were evidently well aware of this property of the bronzes; for their gongs have the composition of these bronzes, and were not cast, but hammered.

Zenghelis has described an ancient bronze coining die found in Egypt in 1904. It dates from 430–322 B.C., and is the only genuine example of an antique bronze die. An analysis of the die showed 69·85 per cent. of copper, 22·51 per cent. of tin, and 7·6 per cent. of oxygen. No impurities were detected, and from the analysis and the relative oxidation of the two metals Zenghelis concludes that the original composition was as nearly as possible 75 per cent. of copper and 25 per cent. of tin.

The die has not been examined microscopically, but there is little doubt that the alloy was quenched in order to enable it to stand the shock of coining.

The influence of annealing on bronze is of some interest and under certain circumstances of considerable practical importance. If the alloys are annealed at temperatures below 500° (that is to say, the temperature at which the δ constituent, or Cu_4Sn, is thrown out of solution), the separation of the two constituents is rendered more complete, and in consequence there is a slight decrease in the tensile strength. If, however, the annealing takes place at temperatures above 500°, the copper absorbs or dissolves more of the δ constituent, and in the case of bronzes of the gun-metal type containing 10 per cent. of tin, the whole of the δ constituent may be dissolved, with the result that an alloy consisting of a single solid solution is obtained. The change is accompanied by a marked increase both in tensile strength and elongation. The maximum effect is obtained at 700°; beyond this there is evidence of incipient fusion, and the alloys develop intercrystalline weakness.

The following tests given by Primrose were made on bars of Admiralty gun metal (88 copper, 10 tin, 2 zinc) cast in chills:—

Temperature of Annealing	Time in minutes.	Tensile Strength in tons per sq in.	Elongation per cent.
..	..	18·6	20·0
500	30	16·7	9·0
600	30	15·0	7·0
650	30	19·5	27·0
700	30	22·5	45·0
750	30	21·0	40·0
800	30	18·6	34·0

Where it is desired to produce a homogeneous alloy possessing great strength and ductility, annealing may be resorted to with advantage, but it must be remembered that a high tensile strength and elongation are not always necessary or even desirable. For example, a gun-metal intended to withstand hydraulic pressure would be improved by annealing, whereas one intended for a bearing or any other machine part subjected to friction would be seriously injured by the same treatment.

Modern bronze nearly always contains small quantities of lead, zinc, and iron, which are often purposely added with the object of conferring special properties upon the bronze. If, however, a combination of strength and elasticity is required, the alloy should be as free as possible from these additions.

Lead, except in very small quantities, does not alloy with bronze, but separates out in the form of minute globules as the metal cools. The best bronzes should not contain more than 0·15 per cent. of lead; but in cases where an alloy of great strength is not necessary, a larger amount of lead is sometimes added, as it enables the metal to be more easily turned or filed. For special purposes, however, a much larger quantity of lead is added. The most important of these are the bronzes used for bearings and for statuary.

Zinc in small quantities has a very beneficial influence when added to bronze. Being an easily oxidisable metal it combines with any oxygen which may be present, either in the free state or in the form of dissolved oxides in the molten metal, with the result that the metal is more fluid—"runs thinner," as it is described, and gives castings free from the defects known as pinholes. A slight excess of zinc will merely alloy with the bronze, without materially affecting its quality; but the excess of zinc should not exceed 2 per cent., otherwise the colour of the bronze will be injured and the alloy will be harder, but weaker.

Iron alloys with bronze, making the resulting alloy lighter in colour and considerably harder. It increases the tenacity, and is useful where a very hard bronze is required.

Bell-metal contains from 15 to 25 per cent. of tin and the remainder copper. Lead, zinc and other impurities should not be present in more than traces in the best metal. Large bells contain the largest amounts of tin, usually about 25 per cent., while small bells contain about 15 per cent. The tone of a bell can be modified to a certain extent by altering its composition, but the purity of tone is a matter which depends more upon the skill of the designer and the founder than upon the composition. In fact, the shape of a bell is of the utmost importance, and it is probable that few metals or alloys could not be used in the manufacture of bells, if they were of the proper shape.

In this connection it is not without interest to recall the fact that as far back as 1726 Lemery noticed that under certain conditions even lead becomes almost as sonorous as bell-metal, and Réaumur, to whom Lemery communicated the fact, subsequently showed that it was necessary to cast the lead in the form of a segment of a sphere. The following table will give an idea of the very variable composition of the alloys used in the manufacture of bells:—

	Copper.	Tin.	Zinc.	Lead.	Antimony.
Large bells . . .	76	24	..	..	...
House bells . . .	78	22	..	...	...
,, ,, . . .	80	20		...	...
Musical bells	84	16	...	...	...
Clock bells .	75	25		...	...
Old bell at Rouen . .	71	26	1·8	1·2	...
Small bells . . .	40	60	...	...	
,, ,, . . .	...	87·5	...	...	12·5

Bell-metal when slowly cooled is very hard and brittle. It consists largely of the compound Cu_4Sn, and is therefore very susceptible to heat treatment. When chilled from a low red heat (*i.e.* at a temperature above that at which Cu_4Sn forms) it is more yellow in colour and malleable.

As regards English bells the earliest existing example to which a date can be affixed is to be found in the village of Claughton, near Lancaster. It is slightly over 16 inches in height, 21 in diameter at the lip, and bears the date 1296 From this time bells with inscriptions and dates are to be found, and the history of bell-founding in this country can be traced. The earliest instructions for bell-founding occur in a treatise by Walter of Odyngton, a monk of Evesham, in the time of Henry III, who describes the method of founding and also the method of determining the relative sizes of the bells necessary to produce the required notes.

Many of the well-known large bells have been recast from older bells. Thus "Great Dunstan" of Canterbury, weighing 3½ tons, was recast in 1762 from an old bell, originally the gift of Prior Molass in 1430. "Bell Harry" was likewise recast in 1635 from an old bell said to have been the gift of Henry VIII. The famous "Great Tom" of Oxford was removed from Oseney Abbey to Oxford at the time of the dissolution of the monasteries, and has passed through many vicissitudes. It was recast in 1612, again in 1654, and in 1680 three unsuccessful attempts to recast it were made, the mould bursting in the third attempt. The next attempt was successful, and the bell was again recast in 1741

Of the more modern and largest bells may be mentioned "Peter" of York, cast by Charles and George Mears at the Whitechapel foundry in 1845. It weighs about 12½ tons, is 7 ft. 4 in. in diameter, and cost £2000.

The original "Big Ben" of Westminster was cast by Messrs Warner & Son in 1856, and weighed 14 tons, with a diameter of 9 ft. It was found to be cracked, and was recast by the Mears at Whitechapel with a slightly reduced weight and a very much lighter clapper—6 cwt. instead of a ton.

"Great Paul" of St Paul's Cathedral was cast at the Loughborough foundry in 1881. It weighs 16 tons 14 cwts. 75 lbs., and has a diameter of 114¾ inches.

Statuary Bronze.—The essential features of a statuary bronze are—(1) that it shall be very fluid and easily cast; (2) that it shall be capable of being finished and easily filed; (3) that its colour shall be as nearly that of gun-metal as is consistent with these requirements; and (4) that under the influence of the atmosphere it shall assume a pleasing oxidation tint or "patina," as it is called.

The alloy which has been found to possess these properties most nearly lies midway between the bronzes and the brasses, and usually contains a considerable percentage of lead. The following table shows the percentage compositions of a number of celebrated statues:—

	Copper.	Tin.	Zinc.	Lead.	Iron.	Nickel.
Column Vendôme, Paris	89·20	10·20	0·50	0·10	...	...
Column of July, Paris	91·40	1·60	5·60	1·40	...	...
Henry IV., Paris	89·62	5·70	4·20	0·48	...	...
Louis IV. equestrian statue, Paris, 1699	91·40	1·70	5·53	1·37	...	...
The Shepherd, Potsdam Palace	88·68	9·20	1·28	0·77	...	...
Bacchus, Potsdam Palace	89·34	7·50	1·63	1·21	0·18	...
Germanicus, Potsdam Palace, 1820	89·78	6·16	2·35	1·33	...	0·27
Mars and Venus, Munich, 1585	94·12	4·77	0·30	0·67	...	0·48
Bavaria, Munich	91·55	1·70	5·50	1·30	...	...
Grosser Kurfürst, Berlin, 1703	89·09	5·82	1·64	2·62	0·13	...
Frederick the Great, Berlin	88·30	1·40	9·50	0·70	...	..
Melanchthon, Wittenberg	89·55	2·99	7·46	...	...	...

The addition of zinc renders the alloy more fluid, and greatly facilitates the operation of casting. Too much zinc, however, should be avoided, or the metal will have a brassy colour, and will not assume a pleasing "patina" on exposure to the atmosphere.

The presence of lead in statuary bronze is very important. In the first place, it appears to give a very fluid metal, but it also causes the bronze to acquire a beautiful brownish black patina, characteristic of many old bronzes on exposure to the atmosphere.

Coinage Bronze.—A bronze which is to be used for coinage must be malleable and ductile, so that it will take the impression of the die; and as hard as possible, in order to withstand wear. In May 1852 France adopted an alloy of 95 per cent. of copper, 4 per cent. of tin, and 1 per cent. of zinc, and the same alloy was first used in England in 1861. It is extremely durable, and is the alloy employed by both countries at the present time. The fact that a large number of the coins struck in 1861 are still in circulation and the date and lettering perfectly legible, is sufficient evidence of the hardness and durability of the alloy.

For medals where fine relief is required a somewhat softer alloy, containing less tin, is used.

Speculum metal derives its name from the fact that it was the alloy employed for the manufacture of reflectors. Until comparatively recently it was used for telescope and other optical reflectors, but these are now made of glass. Speculum metal contains 66·6 per cent. of copper and 33·4 per cent. of tin, and consists of the compound $SnCu_4$. It is extremely hard, brittle, white, and takes a very fine polish. The composition of well-known telescope mirrors varies from 65 to 70 per cent. of copper, the famous Ross reflector containing 68·21 per cent., and the Birr Castle 70·3 per cent.

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CHAPTER VIII.

COPPER ALLOYS, BRASS.

THE discovery of brass vessels and implements of very early origin is proof that the alloys of copper and zinc were known to the ancients; but there is no doubt that, just as in the case of bronze, the early brasses were produced accidentally owing to the admixture of zinc ores with the copper ores. Later on the addition of calamine to copper ores became the regular method of making brass, and was long practised without any knowledge of the part it played in producing the beautifully coloured metal.

There is no doubt that the Romans were the first makers of brass, and the intentional addition of zinc appears to have begun in the time of Augustus (30 B.C. to 14 A.D.), one of the earliest examples being a coin of 20 B.C. which contains 17·3 per cent. of zinc.

The following table gives the composition of several early brass coins:—

	Copper.	Tin.	Zinc.	Lead.	Iron.
Augustus, 30 B.C. to 14 A.D. . .	87·05	0·72	11·80	trace	0·48
Tiberius, 41 to 54 A.D. . . .	72·20	...	27 70	...	...
Nero, 54 to 68 A.D. . . .	77·44	0·30	21·50	trace	0·32
Vespasian, 71 A.D.	81 97	...	18·68	0·14	0·12
Trajan, 98 to 107 A.D. . . .	77·59	0·39	20·70	...	0·27
Sabina, wife of Hadrian, 100 to 137 A.D.	82·35	0·43	16·84	trace	0·38

The early history of brass in this country can be traced by means of the ecclesiastical brasses or *lattens* existing in our churches. Latten was the ancient name of the alloy (which is still retained in the French word *laiton*), and until the middle of the sixteenth century it was manufactured in Flanders and Germany and imported into this country, principally from Cologne, in the form of rectangular pieces known as Cullen plates. The alloy contained considerable quantities of lead and tin, and it is probably on that account that the brasses have lasted so well.

The earliest existing brass is that of Sir John Daubernoun at Stoke d'Abernon in Surrey, and dated about 1277. The brass, 76 in. in length, is in the pavement of the village church, and represents Sir John Daubernoun in a complete suit of chain mail.

From this date onwards there exist a complete series of brasses which have proved of the greatest historical value. Although there are no available analyses of the earliest memorial brasses, several of slightly later date have been analysed and the compositions of a few of these are given in the following table:—

	Copper.	Tin.	Zinc.	Lead.	Iron.
English memorial brass, 14th century	66 64	trace	23·27	...	0·08
,, ,, ,, 1456 . .	67·54	1·16	24 16	7·14	...
,, ,, ,, 1470 . .	66·81	2·56	28 50	2·13	..
,, ,, ,, 1504 .	64·00	3·00	29·50	3·50	...

In the middle of the sixteenth century there is a marked change in the quality of the brass, which now began to be manufactured in England instead of being imported. For the purposes of memorial tablets the English brass was unsuitable, and, according to Mr Macklin, it "was cast, or more probably rolled, in thin plates which have worn grievously."

With regard to the manufacture of brass in England, Haines states that in 1565 Queen Elizabeth granted a patent to Wm. Humfrey, assay master of the Mint, and Christopher Shutz, to search and mine for calamine, and to have the use of it for making all sorts of battery wares, cast works, and wire, of latten. Similar privileges were granted to Cornelius Devoz, Daniel Houghsetter, and Thomas Thurland, and in 1568 the company of the mineral and battery works was incorporated. In 1584 a lease of works at Isleworth was granted to John Brode, and shortly afterwards several other mills were set up.

In 1700 the brass industry was firmly established in this country, and with the success of the famous Cheadle works, which were established in 1730, the industry soon grew to be one of the most flourishing. Owing to the fine colour of the alloy and the ease with which it lends itself to all kinds of mechanical treatment, it has become the most extensively used of the copper alloys. According to its composition, brass may be obtained hard and strong or sufficiently ductile to be drawn into wire or hammered out into sheets whose thickness is not more than $\frac{1}{10000}$ of an inch.

The properties and constitution of the copper-zinc alloys were naturally studied by the early workers, but it is unnecessary to consider their work in detail. The following table, drawn up by the Committee on Alloys appointed by the United States Board, contains in a condensed form the results of investigations down to the year 1881 :—

PROPERTIES OF COPPER-ZINC ALLOYS COLLATED FOR THE COMMITTEE ON ALLOYS APPOINTED BY THE UNITED STATES BOARD (*Report*, vol. ii. 1881).

No.	Atomic Formulæ.	Composition of Original Mixture.		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility (Mallet.)	Relative Ductility. (Thurston.)	Order of Malleability. (Mallet.)	Hardness. (Mallet, Calvert, Johnson.)	Order of Fusibility (Mallet.)	Conductivity for Heat Silver = 100.	Conductivity for Electricity. Silver = 100	Authority.	Remarks.
		Cu.	Zn.	Cu.	Zn.													
1	..	100	0	..	..	8 874	Red.	Fibrous	27,800	8	30·8	..	..	.	..		U.S B.	
2	..	100	0	..	..	8·667	Tile-red.	Earthy	55,104	..	.	1	22	15	..	..	Ml	
3	..	100	0	..	.	8 921	..	..	..	..	.	..			.	93·16	Ma	
4	..	100	0	..	..		..	..		.	..	..	30·1		81·1	..	C. J	
5	..	100	0	..	..	8·952	..	..	.	.	..	.	..			..	Mar.	Sheet copper.
6	..	100	0	..			..	..	.	.	..	.	.	..	73·6	79·3	We.	
7	..	100	0	..	..	8·672	..	..	24,252	.	.	.	.	..	.	..	We.	Mean of nine samples.
8	..	93 15	0·85	..	..	..	..	..	..	..	.			..	.	..	Bo	Tombac for buttons
9	..	97 8	2·2	..	..	.	..	..	.	.		.		..	..	..	.	Red tombac of Vienna.
10	..	97·5	2·5	97·83	1·88	8·791	Yellow-red.	Vesicular	27,240	.	118 9			..	.	.	U S B	
11	..	97·2	2·5	.	..	.	..	..	.	..	..			..	..	..	Bo.	Railway axles porous
12	..	95	5	96 07	3·79	8·825	Yellow-red	Vesicular.	11,500	..	37 9	.	..	..	..	..	U.S B	Defective bar.
13	..	93·6	6 4	..	..	.	..	..	..	..	..	..	..	..	..	..	Bo	Pinchbeck
14	..	92 5	7·5	92·32	7 68	8·746	Yellow-red.	Vesicular.	..	..	.	..	..	.	..	..	U.S B	
15	..	92 5	7·5	..	..	..	..	..	..	..		..	..	..	..	..	Bo.	Bearings, Austria.
16	..	92	8	..	.	..	..	..	..	.	..		..	..	..	..	Bo.	Red tombac of Paris.
17	.	91	9			.		..									Bo	Tombac.

PROPERTIES OF COPPER-ZINC ALLOYS—*continued.*

No.	Atomic Formulæ.	Composition of Original Mixture.		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility. (Mallet.)	Relative Ductility. (Thurston.)	Order of Malleability. (Mallet.)	Hardness. (Mallet, Calvert, Johnson.)	Order of Fusibility. (Mallet.)	Conductivity for Heat Silver=100.	Conductivity for Electricity. Silver=100.	Authority.	Remarks.
		Cu.	Zn.	Cu.	Zn.													
18	$Cu_{10}Zn$	90·72	9 28	..	..	8 605	Red-yellow.	Coarsely crystalline.	27,104	6	..	13	21	14	..	..	Ml.	
19	$Cu_{10}Zn$	90·65	9·35	..	9·60	8·834	..		..	..	..	..	..	..	..	..	Ri.	Specific gravity of ingot 8·753.
20	..	90	10	90·56	9·42	8·773	Yellow-red.	Vesicular.	..	..	169 1	..	..	..	..	..	U S B.	
21	..	90	10	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	French orëide.
22	Cu_9Zn	89·8	10·2	..	..	8·607	Red-yellow.	Finely crystalline	25,760	4	..	11	20	13	..	..	Ml.	
23	..	88·89	11·11	..	..				..	..	..	..	..	..	27·8	25 5	We.	
24	Cu_8Zn	88·6	11·4	..	..	8·633	Red-yellow.	Finely crystalline.	28,672	2	..	10	19	12	..	.	Ml.	
25	..	87·5	12·5	88·94	10·97	..	Yellow-red.	Vesicular.	..	..	..	..	..	..	..	..	U.S.B.	
26	Cu_7Zn	87·8	12·7	..	..	8·587	..	Finely crystalline.	29,568	9	..	9	18	11	..	..	Ml.	
27	..	86·67	13·33	..	..	..	..		..	..	..	..	..	..	29 9	30·9	We.	
28	..	36·38	13·61	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Very delicate castings.
29	..	86	14	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Ornaments of Hanover.
30	..	85·5	14·5	..	..	8·591	Yellow-red.	Fine fibrous	31,584	5	..	8	17	10	..	..	Bo.	French oreide.
31	Cu_6Zn	85·34	14·66	..	..	8·71	..	..	..	..	..	..	..	..	..	..	Ml.	
32	.	85·3	14·7	..	..	..	..	..	..	..	..	..	..	..	..	..	Ri.	Specific gravity of powder 8 584.
33	..	85	15	89·8	10·06	8·656	Red-yellow.	Earthy.	..	..	250·1	..	..	..	..	..	Bo.	Paris jewellery.

34	..	85	15	..	..	..	..	..	..	..	..	..	..	..	..	..	U.S.B.	
35	..	84·6	15·4	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Tombac of Oker.
36	..	84·21	15·79	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Gold-leaf.
37	..	83·9	16·1	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Tombac for buttons.
38	Cu_5Zn	83·02	16·98	..	..	8·415	Red-yellow.	Finely crystalline.	30,688	11	..	2	16	9	..	..	Bo.	Bronze powder.
39	Cu_5Zn	82·95	17·05	..	..	8·673	..	..	..	..	..	..	427·08	..	71·5	..	Ml.	Bath metal.
40	..	82·54	17·46	..	..	..	..	..	..	..	..	..	..	..	..	..	C. J.	
41	..	82·5	17·5	82·93	16·98	8·633	Red-yellow.	Earthy.	32,600	..	105·3	..	..	..	..	..	Bo	Alloy for jewellery.
42	..	82·46	17·54	..	..	..	..	..	..	..	..	..	..	..	31·1	29·02	U.S.B.	
43	..	82·3	17·7	..	..	..	..	..	..	..	..	..	..	..	..	..	We	
44	..	80	20	81·91	17·9	8·598	Yellow.	Earthy.	32,670	..	113·1	..	..	..	..	..	Bo.	Ornaments.
45	Cu_4Zn	79·65	20·35	..	..	..	Yellow-red.	Finely crystalline	52,928	7	..	3	15	8	..	..	U.S.B.	
46	Cu_4Zn	79·56	20·44	..	..	8·650	..	..	..	..	..	..	468·75	..	66·6	..	Ml	Dutch metal.
47	Cu_4Zn	79·51	20·49	..	21·8	8·638	..	..	..	..	..	..	..	..	..	..	C. J.	
48	..	77·9	22·1	..	..	..	..	..	..	..	..	..	..	..	..	..	Ri.	Specific gravity of powder 8·367.
49	..	77·5	22·5	77·39	22·45	8·574	Yellow.	Earthy.	35,630	..	97·5	..	..	..	..	..	Bo.	Vienna gold-leaf
50	..	75·7	24·3	..	..	..	..	..	..	..	..	..	..	..	..	..	U.S.B.	
51	..	75	25	76·65	23·08	8·528	Yellow.	Earthy.	30,520	..	76·7	..	..	..	..	..	Bo	Bristol metal.
52	..	74·62	25·38	..	..	..	..	..	..	..	..	..	..	..	..	..	U.S.B.	
53	Cu_3Zn	74·58	25·42	..	..	8·397	Pale yellow.	Finely crystalline	29,344	10	..	4	14	7	..	..	Ml.	Rolled sheet brass.
54	Cu_3Zn	74·48	25·52	..	..	8·576	..	..	..	..	..	..	468·75	..	63·8	..	C. J.	Brass of thirty-two copper and twelve of zinc.
55	..	72·73	27·27	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	
56	..	72·5	27·5	73·2	26·47	8·465	Yellow.	Earthy.	31,580	..	88·7	..	..	..	..	..	U.S.B.	
57	..	72	28	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Chrysorin.
58	..	71·5	28·5	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Tombac.
59	..	70·1	29·9	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Suitable for forging or leaf.
60	..	70	30	71·2	28·54	8·444	Yellow.	Earthy	30,510	..	77·3	..	..	..	..	..	U.S.B.	
61	..	67·74	32·26	..	..	..	..	..	..	..	..	..	..	..	25·8	25·4	We.	
62	..	67·54	32·46	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Suitable for forging.
63	..	67·5	32·5	69·74	30·06	8·384	Yellow.	Earthy.	28,120	..	48·1	..	..	..	..	..	U.S.B.	
64	..	67·2	32·8	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Bristol metal.
65	..	66·7	33·3	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Chrysorin.
66	..	66·6	33·4	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Common brass.

PROPERTIES OF COPPER-ZINC ALLOYS—*continued.*

No.	Atomic Formulæ.	Composition of Original Mixture.		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility. (Mallet.)	Relative Ductility. (Thurston.)	Order of Malleability. (Mallet.)	Hardness. (Mallet, Calvert, Johnson.)	Order of Fusibility. (Mallet.)	Conductivity for Heat. Silver=100.	Conductivity for Electricity. Silver=100.	Authority.	Remarks.
		Cu.	Zn.	Cu.	Zn.													
67	Cu_2Zn	66·18	33·82	..	.	8·299	Full yellow.	Finely crystalline	28,000	3	..	6	13	6	..	..	Ml.	
68	Cu_2Zn	66·16	33·84	..	..	8·392	..		.	..	..	..	..	..	.	..	Cr.	
69	Cu_2Zn	66·06	33·94	..	..	8·488	..	..	..	472 92	.	..	..	.	62·1	..	C. J	
70	..	66	34	..	..	..	..	..	.	..	..	.	.	.	.	..	Bo	Suitable for forging.
71	..	65·98	34·02	..	34·5	8·41	..	..	.	..	..	.	.	..	..	..	Ri	Specific gravity of powder 8·39.
72	..	65·4	34 6	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo	Good brass wire.
73	..	65 3	34·7	..	..	..	..	..	.	.	.	..	..	..	..	..	Bo	Mosaic gold.
74	..	65	35	66·27	33·5	8·371	Red-yellow.	Earthy	37,800	.	72·8	.	.	..	..	..	U.S.B	
75	..	65	34·76	..	..	..	..	..		..	..	..	..	..	..	..	Bo	Suitable for forging.
76	..	63·5	36·5	..	..	..	..	..	.	..	..	..	..	.	..	..	Bo.	Suitable for forging
77	..	62·5	37·5	63·44	36·36	8·411	Red-yellow.	Earthy.	48,300	..	60 6	..	..	..	..	..	U.S.B	
78	..	61·25	38·75	..	..	..	..	..	..	..	..	..	..	.	..	..	Bo.	Strong solder for brass.
79	..	60·8	39·2	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Bristol metal.
80	..	60·16	39 71	..	..	.	..	..	..	..	..	.	..	..	..	..	Bo	Suitable for forging.
81	..	60	40	60·94	38·65	8·405	Red-yellow.	Earthy.	41 065	.	49	..		..		..	U.S.B	
82	..	60	40	..	..	.	..	..	.	.	.	.	.		..	..	..	Muntz metal.
83	..	59 5	40·5	..	..	..	..	..	.		..	.	.	.	..	..	Bo.	Ship's sheathing.
84	Cu_3Zn_2	59·36	40·64	..	..	8 224	..	..	..	..	.	..	..		..	.	Cr	

85	Cu_3Zn_2	59·26	40·74	..	40 10	8·412	..	..	..	..	..	..	..	..	..	..	Ri.	Specific gravity of powder 8·239.
86	..	58·33	41 77	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Suitable for forging.
87	..	57·5	42 5	58·49	41·10	8 363	Red-yellow.	Earthy.	50,450	..	12·1		..	..	..	..	U.S.B.	
88	..	55	45	..						..		.	..	..	..	..	Bo.	Bath metal.
89	..	55	45	55·15	44 44	8 283	Red-yellow.	Earthy	44,280	..	19·5		..	..	..	..	U.S.B.	
90	..	54 9	45·1	..	..	..	..	..	..	..	.	.	.	..	..	..	Bo.	Very ductile.
91	..	54	46	.	..	..		.	..	..		..	..	..	..	..	Bo.	Very ductile.
92	..	52 5	47·5	54·86	44·78	8·301	Red-yellow	Coarsely granular.	46,400	..	7 4	.	..	..	..	..	U S.B.	
93	..	50	50	49·66	50 14	8 291	,,	,,	30,990	..	3 1	..	..	..	..	..	U S.B.	
94	CuZn	49·47	50 53	..	..	8·230	Full yellow.	Coarsely crystalline	20,608	12	.	5	12	6	..	.	Ml.	German brass
95	CuZn	49 32	50·68	..	..	7 808	..	.	..	..			604·17	.	68 8	..	C J.	
96	CuZn	49·23	50 76	..	50 30	8 304	..	.	..	..	..		.	..	..	..	Ri.	Specific gravity of ingot 8 263
97	..	47·5	52·5	48·95	50·82	8·216	Pinkish grey.	Coarsely granular	26,050	..	·36	.	..	..	..	..	U S.B.	
98	..	45	55	47·56	52·28	..	,,	,,	24 150	.	·26	.	..	..	..	..	U S B.	
99	.	43	57	.	..	..	..	..	.	.		.	..	..	..		Bo	Escutcheons of locks.
100	..	42·5	57·5	43·36	56·22	8·035	Pinkish grey	Finely granular.	9,710	.	·02	..	..	..	.	..	U.S B	
101	..	40	60	41·3	58 12	8·061	Silver-white	Vitreous conchoidal	3,727	.	·01		..	..	..	..	U.S.B.	
102	Cu_2Zn_3	39·27	60·73	..	60·35	8 171	..	..	.	.	..			..	..	..	Ri.	Specific gravity of ingot 8 039
103	..	37·5	62·5	38·36	61·05	7·982	Silver-white.	Vitreous conchoidal.	3,087	..	·02			..	..	..	U S B.	
104	Cu_3Zn_5	36·88	63·12	..	..	7 939	..			.			..	..	..	..	Cr	
105	.	35	65	36·62	62 78	7·974	Silver-white.	Vitreous conchoidal	2,656	.	·006		..	.	..	..	U.S B	
106	$CuZn_2$	33 34	66 66	..	..	..	..	..	.	..	.		..	..	..	..	Bo.	Strong solder for brass
107[1]	$CuZn_2$	32 85	67·15	..	..	8·283	Deep (?) yellow	Coarsely (?) crystalline	43 232?	1	..	7	10	6	..	..	Ml	Watchmaker's brass (?)
108	$CuZn_2$	32·74	67 26	..	..	7 859	.		..	..	..		Broke		42·8	..	C. J	
109	$CuZn_2$	32·66	67 34	..	64·8	8·048	..	..	..	..		.		..	..	..	Ri	Specific gravity of ingot 7 796.

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[1] The properties mentioned by Mallet are wrong. See note on p. 172.

PROPERTIES OF COPPER-ZINC ALLOYS—*continued.*

No.	Atomic Formula.	Composition of Original Mixture.		Composition by Analysis.		Specific Gravity.	Colour.	Fracture.	Tenacity in lbs. per square inch.	Order of Ductility. (Mallet.)	Relative Ductility. (Thurston.)	Order of Malleability. (Mallet.)	Hardness (Mallet, (Calvert, Johnson.)	Order of Fusibility. (Mallet.)	Conductivity for Heat. Silver = 100.	Conductivity for Electricity. Silver = 100.	Authority.	Remarks.
		Cu.	Zn.	Cu.	Zn.													
110	..	32·5	67·5	35·68	63·71	7·966	Silver-white.	Vitreous conchoidal	2,397	..	·11	..	..	..	·	..	U.S.B.	
111	Cu_8Zn_{17}	31·52	68·48	..	..	7·721	,,	Conchoidal.	4,704	0	..	22	5	5	..	..	Ml.	Very brittle.
112	Cu_8Zn_{18}	30·3	69·7	..	..	7·836	,,	Vitreous conchoidal.	4,928	0	..	23	6	5	..	..	Ml.	Very brittle.
113	..	30	70	32·94	66·23	7·811	,,	,,	1,774	..	·005	..	..	..	..	..	U.S.B.	
114	Cu_8Zn_{19}	29·17	70·83	..	..	8·019	Silver-grey.	Conchoidal.	1,568	0	..	21	7	5	..	..	Ml.	Very brittle.
115	Cu_8Zn_{20}	28·12	71·88	..	..	7·603	Ash-grey.	Vitreous.	7,163	0	..	19	3	5	..	..	Ml.	Brittle.
116	..	27·5	72·5	29·2	70·3	7·766	Light grey.	,,	6,414	..	·009	..	..	..	..	..	U.S.B	
		27·1	72·9	..	..	8·058	Silver-grey.	Conchoidal.	2,016	0	..	18	9	5	..	..	Ml.	Brittle.
		26·24	73·76	..	..	7·882	,,	,,	1,792	0	..	20	8	5	..	..	Ml.	Very brittle.
		25·4	74·6	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Protect iron from rust.
		25·39	74·61	..	..	7·443	Ash-grey	Finely crystalline.	13,216	0	..	15	1	5	..	..	Ml.	Barely malleable.
		25	75	..	..	7·675	Bluish-grey.	Finely granular.	9,630	..	002	..	.	..	..	..	U.S B.	..
		24·64	75·36	..	..	7·736	..	..	..	..	..	..	Broke	..	53 1	..	C.J.	..
		24·5	75·5	..	..	7 449	Ash-grey.	Finely crystalline.	11,424	0	..	16	2	4	..	..	Ml.	Brittle.
		22·5	77·5	22·12	77·43	7·416	Bluish grey.	Finely granular.	7,000	..	·004	..	..	..	..	..	U S.B.	..
		20	80	20·31	77·63	7·418	,,	,,	9,000	..	002	..	..	..	..	..	U.S.B.	..
		20	80	..	..	..	..	..	..	..	..	..	..	..	..	..	Bo.	Metal for buttons.

127	$CuZn_4$	19·65	80·35	..	..	7·371	Ash-grey.	Finely crystalline.	4,256	0	..	14	4	3	..	..	Ml.	White button metal.
128	$CuZn_4$	19·47	80·43	..	..	7·445	..	..	..	..	..	..	Broke	..	58·9	..	C. J.	
129	$CuZn_4$	19·52	80·48	..	79·3	7 863	..	..	..	..	..	..	..	..	..	..	Ri	Specific gravity of ingot 7·215.
130	..	17·5	82·5	17·49	81·62	7·225	Bluish-grey.	Finely granular.	5,350	..	·003	..	..	..	..	..	U.S.B.	
131	$CuZn_5$	16·36	83·64	..	..	6·605	Very dark grey.	Finely crystalline.	4,032	0	..	17	11	2	..	..	Ml.	Brittle.
132	$CuZn_5$	16 30	83·7	..	..	7·44	..	..	..	..	..	..	Broke	..	59·5	..	C. J.	
133	..	15	85	14·19	85·1	7·163	Bluish-grey.	Finely granular.	8,500	..	·004	..	..	..	..	..	U.S B.	
134	..	12·5	87 5	12·12	86·67	7·238	,,	,,	12,413	..	009	..	..	..	..	..	U.S B.	
135	$CuZn_8$	10 82	89·18	..	89·9	7·315	..	..	..	..	..	..	..	..	..	..	Ri	Specific gravity of ingot 7·299.
136	..	10	90	10·8	88 88	7·253	Bluish-grey.	Finely granular.	14,450	..	·1	..	..	..	..	..	U.S.B.	
137	..	7·5	92·5	7·2	92·07	7 131	,,	,,	10,650	..	8·04	..	..	..	..	..	U S.B.	
138	..	5	95	4·35	94·57	7 108	,,	Finely crystalline.	18,065	..	·84	..	..	..	..	..	U.S B	
139	..	2·5	97·5	2·45	97·43	7·08	,,	Tabular crystalline.	11,400	..	2 67	..	..	..	..	..	U.S.B.	
140	..	0	100	..	..	7·143	Bluish-white.	,,	5,400	..	26·51	..	..	..	..	..	U.S.B.	
141	..	0	100	..	..	6·895	Bluish-grey.	,,	34,048	..	..	12	23	1	..	..	Ml.	Brittle.
142	..	0	100	..	..	7·148	..	..	..	..	..	..	..	..	29·02	27·39	Ma.	
143	..	0	100	..	..	..	..	..	..	..	..	..	..	..	62 3	..	C. J.	
144	..	0	100	..	..	..	..	..	..	..	..	..	..	..	28 1	27 3	We.	

LIST OF AUTHORITIES REFERRED TO IN PRECEDING TABLE.

Bo.—**Bolley**, *Essais et Recherches Chimiques*, Paris, 1869.

Cr.—**Croockewit**, *Erdmann's Journal*, vol. xlv. 1848, pp. 87-93.

C. J.—**Calvert and Johnson**, *Phil. Mag.*, vol. xviii. 1860, pp. 354-359; *ibid.*, vol. xvii. 1859, pp. 114-121; *ibid.*, vol. xvi. 1858, pp. 381-383.

Ma.—**Matthiessen**, *Phil. Trans*, 1860, pp. 161-184; *ibid*, 1864, pp. 167-200.

Ml.—**Mallet**, *Phil. Mag.*, vol. xxi. 1842, pp. 66-68.

Ri.—**Riche**, *Annales de Chimie*, vol. xxx. 1873, pp. 351-410.

U.S.B.—*Report of Committee on Metallic Alloys appointed by United States Board*, Thurston's investigations.

We.—**Weidemann**, *Pogg. Annalen*, vol. cviii. 1859, pp. 393-407.

Prof. R. H. Thurston, who conducted the investigations for the United States Board, makes the following remarks on the preceding table:—

"Alloys having the name of Bolley appended give compositions and commercial values, and mention valuable properties, such as are given in the column of remarks, but do not give results in figures as recorded by other authorities. The same properties and the same name are recorded by Bolley for alloys of different compositions, such as those which in the column of remarks are said to be suitable for forging. It might be supposed that such properties belonged to those mixtures, and not to others of similar composition. It seems probable, however, that when two alloys of different mixtures of copper and zinc are found to have the same strength, colour, fracture and malleability, it will also be found that all alloys between these compositions will possess the same proportions; and hence that, instead of the particular alloys mentioned only being suitable for forging, all the alloys between the extreme compositions mentioned also possess that property.

"In the figures given from Mallet under the heads of order of ductility, order of malleability, hardness, and order of fusibility, the maximum of each of these properties is represented by 1.

"The figures given by Mallet for tenacity are confirmed by experiments of the author, with a few very marked exceptions. These exceptions are chiefly the figures for copper, for zinc, and for $CuZn_2$ (32·85 per cent. of copper, 67·15 per cent. of zinc). The figures for $CuZn_2$, as given by Mallet, can, in the opinion of the author, only be explained on the supposition that the alloy tested was not $CuZn_2$, but another containing a percentage of copper, probably as high as 55. The figure for the specific gravity (8·283) given by Mallet indicates this to be the case, as also does the colour.

"The figure for ductility would indicate even a higher percentage of copper. The name watchmaker's brass in the column of remarks must be an error, as that alloy is brittle, silver-white and extremely weak.

"The figure of Calvert and Johnson and Riche, as well as those of the author, give a more regular curve than can be constructed from the figures of Mallet.

"The specific gravities in Riche's experiments were obtained both from the ingot and from powder. In some cases one, and in some cases the other, gave highest results. In the table under the head of specific gravity Riche's highest average figures are given, whether these are from the ingot or from the fine powder as probably the most nearly correct. The figures by the other method, in each case, are given in the column of remarks.

"The figures of Riche and Calvert and Johnson are scarcely sufficient in number to show definitely the law regarding specific gravity to composition, and the curves from their figures vary considerably.

"The figures of the author being much more numerous than those of earlier experimenters, a much more regular curve is obtained, especially in that part of the series which includes the yellow or useful metals. The irregularity in that part of the curve which includes the bluish-grey metals is, no doubt, due to blowholes, as the specific gravities were in all cases determined from pieces of considerable size. If they were determined from powder, it is probable that a more regular set of observations could be obtained, and that these would show a higher figure than 7·143, obtained from cast zinc. Matthiessen's figure for pure zinc (7·148) agrees very closely with that obtained by the author for the cast zinc, which contained about 1 per cent. of lead.

"The figures for hardness given by Calvert and Johnson were obtained by means of an indenting tool. The figures are on a scale in which the figure for cast iron is taken as 1000. The alloys opposite which the word 'broke' appears were much harder than cast iron; and the indenting tool broke them, instead of making an indentation. The figures of alloys containing 17·05, 20·44, 25·52, and 33·94 per cent. of zinc have nearly the same

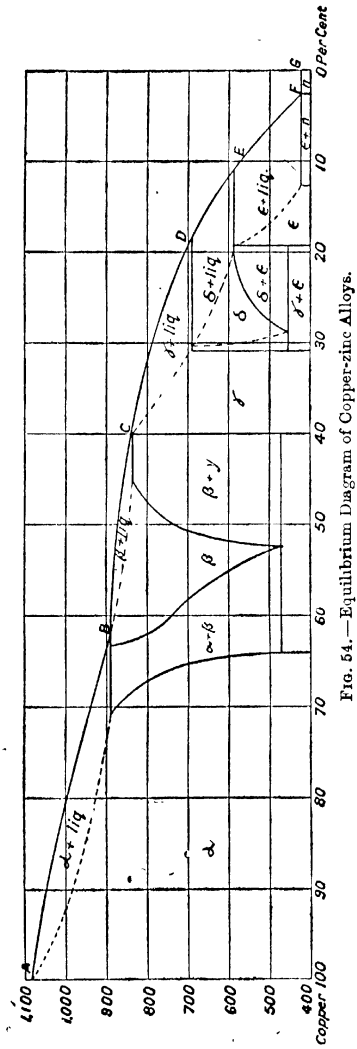

FIG. 54.—Equilibrium Diagram of Copper-zinc Alloys.

figures for hardness, varying only from 427·08 to 472·92. This corresponds with what has been stated in regard to the similarity in strength, colour, and other properties of alloys between these compositions."

Since the publication of this table much has been added to our knowledge of the brasses by the work of Charpy, Roberts-Austen, Behrens, Le Chatelier, and many others. The melting-points of the copper-zinc alloys have been determined by Charpy and Roberts-Austen, and their work has been confirmed and amplified more recently by Shepherd, Tafel, and Carpenter and Edwards, from whose results the adjoining diagram (fig. 54) has been drawn. This equilibrium diagram expresses all that is at present known of the constitution of the copper-zinc alloys. For the sake of comparison curves representing the mechanical properties of the copper-zinc alloys are plotted in fig. 55, which should be read along with fig. 54.

Most writers have concluded that copper and zinc form a definite compound corresponding to the formula $CuZn_2$, and, possibly, other compounds corresponding to CuZn and $CuZn_4$. Shepherd, on the other hand, argues that copper and zinc form six solid solutions, but do not form any definite compound. This opinion is difficult to reconcile with the very strong evidence which has been brought forward in support of the view that a compound $CuZn_2$ exists. Briefly, the experimental evidence in support of the existence of a compound is as follows:—(1) There is a rapid diminution in the strength of the alloys as the composition $CuZn_2$ is reached. (2) The alteration in the electromotive force of the alloys, as shown by Laurie in 1888, and later by Herschkowitsch, points to the existence of a compound. (3) The

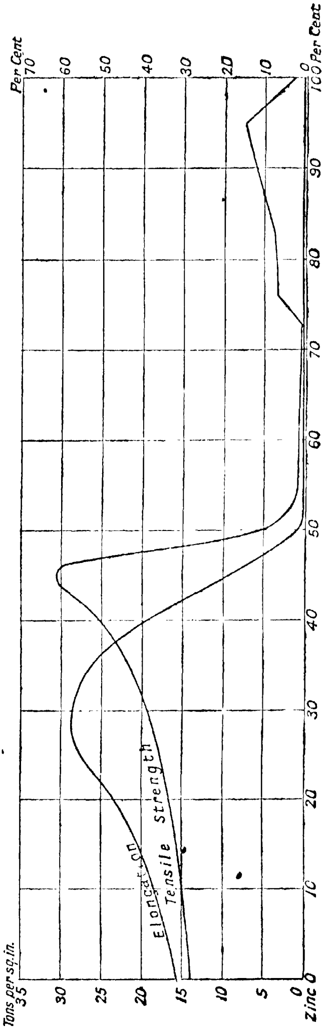

FIG. 55.—Mechanical Properties of Copper-zinc Alloys.

electrical resistance of the alloys shows a sudden variation at the same point, as also do the curves of temperature coefficient and thermo-electric power; and, finally (4), both Baker and Herschkowitsch have shown that the heat of formation of the alloys reaches a maximum at the point corresponding to the composition $CuZn_2$. This maximum amounts, in Baker's experiments, to 52·5 calories per gram of the alloy, and his results also show a second rise at a point corresponding to the formula CuZn.

It is true that the microscopical examination of the alloys shows a continuous series of apparently solid solutions, but it must be remembered that Charpy has shown that compounds and solid solutions may be mutually soluble in one another, and this would be quite sufficient to account for any lack of discontinuity in the microstructure of the series.

A glance at the freezing-point curve of the series will show that the constitution of the alloys rich in zinc is very complex, but these alloys are of little industrial importance, and the constitution of the alloys rich in copper—that is to say, the brasses—is comparatively simple. With a few exceptions the alloys of industrial value may be said to lie within the limits of 55 and 70 per cent. of copper. The alloys containing more than 64 per cent. of copper consist of a single homogeneous solid solution, while those containing from 55 to 64 per cent. of copper are composed of two constituents, each of which is a solid solution. Photograph 12 shows the appearance of a brass containing 70 per cent. of copper, and photograph 13 is a typical yellow brass or Muntz metal. The alloys with the simple structure can be rolled cold (although in practice they are more often rolled hot), while those containing two constituents are rolled hot. Of course there is no sharply defined limit between the alloys which can be rolled hot and those capable of being rolled cold, but they can be classified in a general way according to their structure.

The early or calamine method of making brass, which has been referred to, consisted in heating a mixture of zinc oxide, charcoal or coal dust, and granulated copper in crucibles. The zinc oxide was reduced by the charcoal and the liberated metal then alloyed with the copper, forming brass. This process has, however, long been abandoned in favour of a direct method, and is now only of historical interest. At the present time brass is made by the direct fusion of the metals, the copper being melted first under a layer of charcoal to prevent oxidation and the zinc added to the molten metal at as low a temperature as possible. The alloy is then stirred and, if necessary, allowed to cool somewhat before pouring. The melting is nearly always carried out in crucibles, usually of plumbago, heated in furnaces, which may be either coke-, oil-, or gas-fired. Where large ingots of yellow brass or Muntz metal are required, the alloy is sometimes made in reverberatory furnaces, capable of melting several tons of metal; but the loss of zinc in reverberatory melting is very high, and the method is not employed for high-grade brasses.

The pouring or casting of the melted alloy is a very important operation, as the quality of the brass depends largely on the temperature at which it is carried out. If the temperature is too high it will be full of blowholes and will probably crack in rolling. Such defective metal is sometimes described as "spuey." If, on the other hand, the metal is poured at too low a temperature it tends to solidify as it touches the mould, with the result that there is imperfect cohesion of the metal, or, as the melter describes it, it is "spilly." This term is also applied to imperfect castings due to the presence of charcoal or dross. The moulds into which the metal is poured are previously heated and the insides coated with oil or mixtures of charcoal and oil or resin and oil.

The industrial brasses may be conveniently divided into three classes, viz. :—

1. Cast brass.
2. Low brass for hot rolling.
3. High brass for cold rolling.

Cast brass is very variable in composition, but, with the exception of a few alloys rich in copper used in the manufacture of cheap jewellery, etc., the usual composition of cast brass is in the neighbourhood of 66 per cent. of copper and 34 per cent. of zinc, which is known as English standard brass. It casts well, and is capable of being rolled and hammered and even drawn into wire. In most cases, however, cast brass is not required to undergo much mechanical treatment, and it is consequently very impure. Large quantities of scrap are employed in its manufacture, and it usually contains relatively large amounts of impurities, such as tin, iron, and lead. These are of little consequence, and, in fact, if the metal is to be machined or filed the presence of lead, as will be seen later, is a distinct advantage in facilitating these operations. Further, the presence of tin and lead together gives rise to very fluid alloys invaluable for fine castings, and having a colour somewhat resembling bronze.

Low brasses, suitable for hot rolling, contain from 55 to 63 per cent. of copper. They are cast in large ingots, which are reheated and passed through the breaking down rolls, followed by a second reheating before passing through the finishing rolls. Hot rolling is therefore rapidly carried out, and only requires a single reheating from beginning to end of the rolling.

The commonest of the yellow brasses is that known as Muntz metal. In 1832 George Frederick Muntz took out a patent[1] for the use of an alloy containing 60 per cent. of copper and 40 per cent. of zinc as a sheathing metal for ships, and he claimed that in these proportions, "whilst the copper was to a considerable extent preserved, there was a sufficient oxidation to keep the bottom of a ship clean." In 1846 Muntz took out another patent for a cheaper alloy containing 3½ per cent. of lead and 56 per cent. of copper, which was claimed to be equally satisfactory for the purpose. Although these alloys are no longer required for the particular purpose for which the patents were issued, the alloy containing 60 per cent. copper and 40 per cent zinc is largely used for other purposes, and is still known under the name of Muntz metal.

As already mentioned, Muntz metal contains two constituents —a soft constituent α and a harder constituent β. In the cast state the alloy possesses a coarse structure, the two constituents separating in large masses, but the effect of hot rolling is to retard the growth of these masses with the production of a stronger metal possessing a finer structure. If the work takes place at temperatures below 600° the alloy is no longer capable of any molecular re-arrangement, and the only effect is to distort the grains or crystals already formed. A temperature of 600° is therefore regarded by Bengough and Hudson as the limiting temperature dividing "hot" and "cold" work for this particular alloy. The effect of cold work is removed by annealing at about 800°, or by prolonged annealing at lower temperatures.

Muntz metal is hardened by quenching, and the explanation of this is readily seen from its structure. With increasing temperature the α constituent is dissolved by the harder β constituent until, at 720°, the alloy containing 60 per cent. of copper consists entirely of the β constituent. If, now, the alloy is quenched from this temperature the separation of the α constituent is hindered, and the alloy will be found to be stronger, but less ductile than before.

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[1] Pat. No. 6325.

High brasses, suitable for cold rolling, usually contain more than 60 per cent. of copper, and the best class of brass for tubes and wire drawing contains 70 per cent. of copper and 30 per cent. of zinc. From the results of mechanical tests it will be seen that this alloy possesses the maximum elongation of the series combined with a considerable degree of strength.

Brass intended for rolling or drawing is cast in moulds of such shape that the work required on the alloy shall be reduced as far as possible. For plate or wire the moulds, which are made of iron, are from ⅝ to ⅞ of an inch thick, 3½ to 12 ins. wide, and 18 to 28 ins. long. They are made in two pieces held together by the simple device of a ring and wedge. For wire drawing the plates cast in these moulds are rolled to a certain extent and then cut into strips, which are rolled into rods and finally drawn into wire. In any case, the mechanical treatment of brass in the cold must be interrupted by frequent annealing, or the results will be disastrous. Moreover, after each annealing the brass has to be cleaned in acid to remove the surface deposit of oxide. As an instance of this, Sir William Anderson states that in the production of a brass cartridge case, measuring 16 ins. in length and tapering from 7 ins. diameter at the breech end to 6½ ins. at the muzzle end, made from a disc of brass 12⅝ ins. in diameter by ¾ ins. in thickness and weighing 28¾ lbs., no less than eight annealings and cleanings in acid are necessary during the stages of drawing. If an attempt is made to lessen the number of annealings the alloy in the finished product is in a state of molecular strain, and the effort of the metal to return to its natural state of equilibrium results, in the course of time, in the fracture of the metal. Instances of cartridge cases cracking in this manner while in the arsenal stores caused considerable trouble until the cause was discovered. This cracking, which may not take place until many months after the manufacture of the article, is known as "season" cracking, and is very liable to occur in drawn tubes if the pinch has been too great and the annealing insufficient. In an actual case under observation a tube was noticed, three months after the date of manufacture, to be slightly elliptical in section. After six months the effect was exaggerated, and not until one year had elapsed did the tube actually crack. The cracks always occur longitudinally, and the average time of appearance is from six to twelve months after manufacture. Season cracking is also liable to occur in spun brass.

The annealing of brass is carried out in reverberatory furnaces, which may be heated by solid or gaseous fuel; but in either case the object aimed at in the construction and working of the furnace is to maintain a reducing atmosphere so as to cause a minimum of oxidation. The temperature of annealing is of great importance, and much light has been thrown on the subject by the work of Charpy. He experimented on brasses of varying composition, which were hammered and rolled until a maximum hardness was reached. Mechanical tests were made on these brasses in their hardened condition, and also after annealing at gradually increasing temperatures. The results show that up to a certain temperature annealing is without effect. Above this temperature (which is not absolutely fixed, but depends on the amount of hardening the alloy has undergone) the effect of annealing increases with the increase in temperature until a maximum is reached. Above this point there is a range of temperature at which the properties of the brass remain unaltered, but beyond the upper limit of this range the alloy rapidly deteriorates and is said to be burnt. The figures obtained from the annealing of a brass containing 70 per cent. of copper and 30 per cent. of zinc may be taken as an example (see p. 181).

It will be seen that annealing below 280° has practically no effect. At 420°, however, there is a very marked softening of the alloy, and the maximum effect of annealing is reached at 600°. According to Charpy the alloy made from pure copper and zinc can be annealed at a temperature of 900° without being burnt, but the same brass containing 0·15 per cent. of tin and 0·2 per cent. of lead is burnt at about 800°. The mechanical properties of the series of alloys in a completely annealed condition containing from 0 to 50 per cent. of zinc have been determined, and the results of the tensile tests and elongations are plotted in the curves in fig. 55. Tests on the compressive strength of the alloys showed that this property varies inversely as the elongation, and the results of shock tests showed that with alloys containing less than 43 per cent. of zinc the fragility was negligible, but beyond this limit the alloys rapidly became brittle, and those containing more than 50 per cent. of zinc broke with the slightest shock. From these results Charpy concludes that as far as the mechanical properties of the brasses are concerned the alloys should not contain more than 45 per cent. of zinc, and that no useful purpose is served by having less than 30 per cent. of zinc.

Annealing Temperature.	Tensile Strength in tons per sq. in.
0	31·4
200°	32·5
280	29·5
420	21·6
500	21·6
560	19·0
600	17·4
650	17·4
730	18·6
780	18·2
800	18·2
850	17·4

The influence of prolonged annealing on brasses containing more than 65 per cent. of copper is of considerable interest. The structure of these alloys in the cast state consists of crystallites resembling those of bronze, but if the metal is annealed at about 600° the structure gradually changes, the crystallites disappearing and giving place to a well-defined crystalline structure resembling that of a pure metal. With prolonged annealing these crystals increase in size; and if a sample of commercial rolled brass, whose structure consists of small crystals, is annealed, the crystals will attain a considerable size; but in this case the result of the mechanical treatment which the metal has undergone is made evident by the appearance of "twin" crystals. The large crystals are composed of a homogeneous solid solution, and are themselves structureless.

Brass is capable of withstanding very drastic treatment, and in addition to rolling, drawing, stamping, and spinning, it is capable of being extruded or forced through dies at temperatures somewhat below the melting-point of the alloy. Great advances have been made within the last few years in the extrusion of brass, and complicated sections which it would be impossible to roll are now regularly manufactured by this process.

Up to the present we have regarded brass as a simple alloy of copper and zinc; but commercial brass invariably contains other metals, and, although they are only present in small quantities, their presence has an important influence upon the quality of the brass. It is therefore necessary to consider them in some detail. Some of these metals are added intentionally in order to confer certain properties upon the alloy, and others occur as impurities. Those added intentionally are lead, tin, and iron, while lead, arsenic, antimony, and more rarely bismuth, are introduced unintentionally.

Lead.—Brass is never entirely free from lead, as the zinc employed in its production invariably contains a small percentage of lead. High-grade brass, however, should never contain more than 0·10 per cent. of lead or its ductility will be impaired. In the case of brasses which are to be turned or machined lead is added intentionally, and the object of the addition is readily apparent when the structure of the brass is considered. Lead does not alloy with brass, but separates out in the form of globules and films between the crystals of the brass, a condition which necessarily weakens the metal, and is only permissible where strength is of secondary importance. The presence of 2½ or 3 per cent. of lead cannot be detected in a polished surface without the aid of a microscope; but if the brass is broken the fracture is of a distinct grey colour, owing to the fact that the line of fracture passes through the lead. Now, it is well known that a pure brass is difficult to turn owing to the nature of the turnings, which are long and tenacious, and tend to obstruct the mechanism of automatic machines. A slow speed has to be employed, and frequently a burr is produced which is difficult to remove. Brass containing lead, however, behaves very differently Owing to the fact that the lead is in a free state, the alloy is less tenacious, and the turnings break off through the lines of weakness caused by the lead, so that chips are produced instead of long spiral turnings. Moreover the lead appears to act as a lubricant, with the result that a much higher speed can be employed, and a better finish given to the work.

The beneficial effect of lead in brasses intended for turning was known long before the nature of its influence was understood. Percy states that it is usual to introduce a small quantity of lead (about 2 per cent.) into brass in order that the chips may leave the tool easily. He mentions that the lead should be added after the crucible has been withdrawn from the fire; but the usual method is to add the lead after the zinc, and while the crucible is still in the fire, yet at as low a temperature as possible. In any case, the alloy is thoroughly stirred immediately before pouring.

The alloy is rolled cold, on account of its liability to crack if rolled hot, and the amount of lead which can be added, without seriously affecting it as regards its capability of being rolled, is about 2 per cent. The best alloy, and that which is most commonly used, contains about 60 per cent. of copper, 38 per cent. of zinc, and 2 per cent. of lead. Three samples of hard drawn screw-rods quoted by Sperry gave the following mechanical tests:—

	I.	II.	III.
Tensile strength per sq. in.	64,500 lbs.	62,400 lbs.	54,000 lbs.
Elongation on 8 ins.	10 per cent.	13 per cent.	26 per cent.
Reduction of area	58 ,,	63 ,,	53 ,,

Tin should not be present, as it imparts hardness and strength to the alloy, properties which are not aimed at in a brass intended for turning.

Tin.—This metal is often added to brass, and the alloy is known as "naval" brass. A small percentage of tin renders brass, and more especially low brasses of the Muntz metal type, less liable to corrosion by sea water when in contact with gun-metal. It is for this reason that brasses containing tin are employed in naval construction. Naval brass contains approximately 62 per cent. of copper, 37 per cent. of zinc, and 1 per cent.

of tin, while a softer alloy, suitable for tubes, etc., which has given good service, contains 78 per cent. of copper, 21 per cent. of zinc, and 1 per cent. of tin.

The addition of 1 per cent. of tin to brass gives an increase in the hardness of the alloy, but does not seriously affect its mechanical properties. Beyond this limit, however, there is a rapid increase in brittleness and hardness; and with more than 2 per cent. the alloys lose their useful properties.

Arsenic and Antimony.—Commercial copper usually contains these metals as impurities. Their presence has an important influence on the quality of the brass produced. Antimony appears to be more injurious than arsenic, and, even in small quantities, is capable of rendering brass unfit for rolling on account of cracking.

Sperry found that as little as 0·02 per cent. of antimony in an alloy of 60 per cent. copper and 40 per cent. zinc gave rise to incipient cracks during the necessary annealing and rolling.

Bismuth also occurs, though more rarely, in some qualities of commercial copper, and hence finds its way into brass. Its effect is very similar to that of antimony, but, according to Sperry, it is less injurious. For example, he found that brass composed of 60 per cent. copper and 40 per cent. zinc containing 0·02 per cent. of bismuth rolled almost as well as pure brass and was free from cracks. Sperry, therefore, gives this figure as the dividing line between good and bad brasses of this composition; but he states that high brasses intended for cold rolling should not contain more than 0·01 per cent. of bismuth.

It is not difficult to understand the nature of the behaviour of these impurities. Neither antimony nor bismuth is appreciably soluble in copper or in copper-zinc alloys. The result is that when the brass cools down and solidifies, the antimony and bismuth (either in the free state or containing small quantities of copper), having much lower melting-points than the brass, remain liquid, and finally solidify between the crystals of the brass. Consequently, each grain or crystal of the brass is separated from its neighbour by a thin, brittle film, and when the brass is rolled these separating layers are incapable of withstanding the strain, and the alloy cracks. Arsenic, on the other hand, is distinctly soluble in copper, and is therefore less harmful. In fact, it has a hardening effect upon the copper, and its presence is sometimes actually beneficial, provided the limit of solubility is not exceeded. As a rule 0·5 per cent. is considered the maximum.

Iron has been added to brass from early times, but it is probable that its presence in old brasses was accidental At the present time, however, iron is deliberately added to brass in order to produce a stronger and harder alloy than ordinary brass An alloy containing close on 3 per cent. of iron was suggested by Keir in 1779, and later the alloys known as sterro metal and **Aich's metal**[1] were introduced.

Sterro metal contains 60 per cent of copper, 38 per cent of zinc, and 1·5 to 2 per cent. of iron, and Aich's metal is practically the same, although various analyses show that the percentage of iron varies within wide limits.

One of the few reliable tests of these alloys is given by Baron Rosthorn, who tested a sample of sterro metal containing 55·01 per cent. of copper, 42·36 per cent. of zinc, 0·83 per cent of tin, and 1·77 per cent. of iron, with the following results:—

Condition.	Tenacity in lbs. per sq. in.
Cast . . .	60,480
Forged . . .	76,160
Cold drawn . . .	85,120

The very variable percentages of iron found in these alloys was probably due to the imperfect methods of manufacture, the iron being added in the form of a copper-iron alloy which was in all probability not properly alloyed. In 1883, however, Alexander Dick took out a patent[2] for the manufacture of iron brass which he called **Delta metal,** and since that time these alloys have been largely used.

The essential features of Dick's patent were—

(1) The introduction of the iron in the form of an alloy of iron and zinc, which could be obtained of reliable composition, and (2) the addition of a small percentage of phosphorus, which has the effect of preventing oxidation.

In addition to iron and phosphorus, however, commercial Delta metals frequently contain manganese, aluminium, tin, and sometimes lead, which accounts for the different compositions as shown by various published analyses of these alloys.

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[1] Patented 1860, No 278.

[2] No. 2484.

The average composition is approximately copper 55 per cent., zinc 42 per cent., with 1 to 2 per cent. of iron and small quantities of manganese, aluminium, etc.

Delta metal is stronger, harder, and tougher than brass. It is easily cast, and is capable of being rolled hot and drawn cold. In addition, it has a much greater power of resisting corrosion than ordinary brass, which enables it to be used for many purposes where brass is inadmissible.

The table on p. 149 gives some results of tests made at Lloyd's on samples of Delta metal.

Delta metal was employed for the manufacture of the worm wheels in the first locomotives used on the Pilatus mountain railway and gave very satisfactory results, as reported in the *Schweizerisches Gewerbeblatt* of 8th June 1889. The castings, which were tested by Prof. Tetmayer, showed a tensile strength of 21½ to 23½ tons per sq. in., with an elongation of 30 to 40 per cent. on a length of 7⅞ ins.

An iron brass under the name of **Durana metal** is manufactured in Germany. It appears to closely resemble Delta metal in its properties, and is made in several qualities. Tests on a number of samples of this alloy gave results varying between 23 and 43 tons per sq. in. ultimate stress and 7½ to 38 tons elastic limit, with elongations of 50 and 4½ per cent. respectively on a length of four inches.

The constitution of the iron brasses has not been sufficiently investigated, but when present in small amounts the iron enters into the alloy in the form of a solid solution and does not form definite chemical compounds. When more than about 2 per cent. of iron is present a compound of iron and zinc is formed.

The majority of the commercial brasses are considerably complicated owing to the presence of manganese and aluminium in addition to the iron, and there is an increasing tendency at the present time to use brasses of a complex nature in preference to those containing, in addition to the copper and zinc, a single metal such as iron, manganese, or aluminium.

[TABLE.

Mark on Test.	Description.	Size and Specimen.	Original Area. Sq. in.	Fractured Area. Sq in.	Permanent Set in tons per sq. in.	Maximum Stress in tons per sq. in.	Elongation per cent. in 8 ins.
No. 1	Square bar annealed	·5 dr. turned	·1963	·1288	Not taken.	27·8	39
No. 2	**Flat plate annealed**	1·44 × ·128	·1843	·1102	12·1	30·0	36
No. 3	**Round bar**	·495 dr. turned	·1924	·1352	23·4	32·1	23
No. 4	**Hexagonal bar**	·49 dr turned	·1885	·1256	25·0	31·3	11 Broke in extension mark.
No 5	**Flat plate**	1·44 × ·128	·1843	·1620	13·7	35·4	14

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CHAPTER IX.

COPPER ALLOYS SPECIAL BRONZES AND BRASSES

Phosphor-bronze.

THE addition of phosphorus to bronze has usually been attributed to Dr Kunzel of Dresden, but it appears that De Ruolz and De Fontenay had carried out experiments on the introduction of phosphorus into bronze as early as 1853.

Phosphorus unites both with copper and tin, forming the alloys known as *phosphor copper* and *phosphor-tin* (see Chap X), which are used as the means of introducing the phosphorus into bronze.

The action of phosphorus on copper or bronze is a double one. In the first place, as is well known, phosphorus has a powerful affinity for oxygen, and when it is added in the form of phosphor-copper or phosphor-tin to the molten metal, its first action is to reduce any oxides which may be present The oxide of phosphorus thus formed has an acid character and combines with a further quantity of metallic oxides forming phosphates, which pass into the slag.

The bronze, which is now free from the dissolved oxides which cause so much trouble, is more fluid, gives castings free from pinholes, and is superior in every way to ordinary bronze.

If the quantity of phosphorus has been accurately judged, none of it will pass into the bronze; and this accounts for the fact that many excellent bronzes sold as phosphor-bronzes have failed to show the presence of phosphorus when submitted to chemical analysis. Their superiority over bronzes produced without the addition of phosphorus is entirely due to the removal of dissolved oxides.

The value of phosphorus as a deoxidiser is now fully appreciated, with the result that its importance as a constituent of bronze has been considerably underrated and misunderstood. It has frequently been stated that the only use of phosphorus is as a deoxidiser, and that when the quantity present is in excess of that necessary to destroy the oxides in the alloy the bronze is inferior in quality. This statement requires considerable modification, as in many cases an excess of phosphorus is purposely added, and is found to confer valuable properties upon the alloy. The mistake, however, has probably arisen from the fact that the bronzes containing phosphorus have very different properties to those of ordinary bronze, and are very frequently not adapted to the same purposes.

The term phosphor-bronze is applied to many alloys, and to avoid confusion these may be grouped into three classes :—

1. Bronzes of ordinary composition, in which phosphorus has been employed solely as a deoxidiser, not more than a trace being present in the bronze.

2. Bronzes containing less than 9 per cent. of tin and only traces of phorphorus. These are frequently put on the market as "Rolled or Malleable Phosphor-Bronze."

3. Bronzes containing more than 9 per cent. of tin and an excess of phosphorus (usually from 0·2 to 2 0 per cent.), and sold as "Cast Phosphor-Bronze." Among this group may be placed the bronzes containing phosphorus and lead used as bearing metals.

The bronzes in Class 1 call for no special remark, as they are merely ordinary bronzes free from oxides. Those of Class 2 can be employed for all purposes for which copper and soft bronzes are used, such as boiler tubes, condenser tubes, pump rods, piston rods, boiler stays, firebox stays, bolts, nuts, etc. When cold rolled these bronzes show a breaking strain as high as 30 tons per sq. in. or even more, with an elastic limit of about 26 tons per sq. in.; while the same bronzes, after annealing, give a breaking strain of 20 tons per sq. in. and an elastic limit of about 7 tons per sq. in.

Rolled phosphor-bronze is also used for making boiling vats, tanks, stills, and parts of machinery working in liquids, on account of its superior resistance to corrosion.

At first sight it appears strange that these bronzes should resist corrosion better than ordinary bronzes, considering that they are of exactly the same composition; but the resistance to corrosion is due to the absence of oxide in the metal; for it must be remembered that such impurities have a very decided influence on the rate of corrosion. This subject will be considered at greater length in another chapter.

Rolled phosphor-bronze does not suffer any serious loss of strength at temperatures up to 300° C., and it is frequently recommended for firebox plates and stays.

The following table gives some results of tests made upon two well-known brands of rolled phosphor-bronze:—

Sample.	Condition.	Breaking Stress. Tons per sq. in.	Elastic Limit. Tons per sq. in.	Elongation per cent. on 2 ins.
1	Unannealed sheet	28·3	25·0	18·5
2	,, ,,	33·8	31·5	17·0
3	,, ,,	31·9	31·7	17 5
4	Annealed sheet	20·3	7·8	57 0
5	Sheathing plate	30·1	...	18·7
6	Bolt	28·8	27·5	26·6
7	Loco. firebox plate annealed	20 0	...	64·06

Samples 1 to 4 are by the Phosphor-Bronze Company, and samples 5 to 7 are "Melloid," by Bull's Metal and Melloid Company.

Much depends, of course, on the extent of the rolling; but by way of comparison it may be taken that the breaking stress of copper varies from 13 tons per sq. in. in the annealed condition to about 18 tons per sq. in. when rolled.

As regards the tensile strength of rolled phosphor-bronze at elevated temperatures, experiments carried out on a "Melloid" bolt showed that the breaking stress fell from 28·82 tons per sq. in. at the normal temperature to 25·51 tons per sq. in. at 315°. On an annealed bolt of the same material the breaking stress fell from 19·22 tons per sq. in. at the normal temperature to 18·80 tons per sq. in. at 214°; while a similar bar of copper, tested under the same conditions, fell from 13·84 to 10·25 tons per sq. in.

From what has been said of the constitution of the copper-tin alloys it will be seen that the rolled phosphor-bronzes which have been placed in Class 2 are solid solutions, and exhibit a simple crystalline structure under the microscope.

The phosphor-bronzes of Class 3 differ considerably from those of Class 2 and also from those of Class 1. Their constitution is somewhat complex, but of considerable interest. M. Guillemin pointed out in a communication to the Commission des Méthodes d'Essai in 1894 that under the microscope phosphor-bronzes exhibit a structure resembling a fern leaf or fir branch, and that this structure is not easily confounded with an ordinary bronze. It is doubtful, however, whether this can be regarded as the invariable structure of phosphor-bronzes, as sometimes the structure of ordinary bronze resembles it very closely. Guillet states that the phosphorus appears to enter into the α solution (*i.e* the solution of tin in copper containing less than 9 per cent. of tin). If the alloys are examined under a high magnification it will be seen that this is not the case, but the reason of the mistake will also be apparent It has already been shown that in bronzes containing more than 9 per cent of tin a constituent δ ($SnCu_4$) separates out on cooling, and that this constitutent is of a pale bluish-white colour. Now, if an access of phosphorus is present in such an alloy it separates out on cooling in the form of phosphide of copper, which has very nearly the same colour as the $SnCu_4$ constituent, but slightly darker in shade. Moreover, these constituents occur side by side (in fact, they form a eutectoid), and unless seen under a high magnification they appear as one constituent. On account of the similarity in colour it is extremely difficult to obtain a photograph, but by using a suitable screen it is possible. Photographs 14 and 15 show the fern-like structure referred to by Guillemin, and photograph 16 shows the combination of $SnCu_4$ and phosphide existing partly as eutectoid. This triple eutectoid of the series contains 81·0 per cent. copper, 14·2 per cent tin, and 4·8 per cent. phosphorus, with a melting-point of 620°. The eutectoid of the two compounds is shown in photograph 18.

By means of heat-tinting, the different constituents can be readily distinguished; the phosphide colouring a beautiful blue, while the $SnCu_4$ is coloured yellow (photograph 17, and frontispiece).

The presence of free phosphide of copper in these bronzes accounts for their properties, differing as they do from ordinary bronze, and is sufficient to explain their great value for certain purposes. If, for example, a phosphor-bronze is subjected to friction, it is obvious that the softer part of the alloy will be worn down, leaving the hard phosphide in relief. The alloy thus consists of intensely hard particles imbedded in a softer matrix, so that not only is the wearing surface largely decreased and the friction consequently reduced, but the rate of wear is practically the rate of wear of the hard body, phosphide of copper. Phosphor-bronze is therefore peculiarly adapted for the manufacture of the wearing parts of machinery, such as bearings and bushes, worms and worm wheels, slide faces, piston rings, etc., and has a much longer life than ordinary bronze. Moreover, as the hard particles of phosphide are set in a matrix or cement of a comparatively plastic material, the alloys are not as brittle as might be expected, but are capable of withstanding considerable shocks, and will suffer distortion without breaking.

The main feature, then, of phosphor-bronze is its remarkable hardness and resistance to wear, and it would appear that for parts of machinery subject to wear there is no alloy to surpass it. The effect of the addition of phosphorus to the copper-tin alloys is worthy of a little attention. Guillet has made a number of tests on bronzes, the results of which are embodied in the following table:—

Composition.			Tensile Strength Tons per sq. in.	Elastic Limit Tons per sq. in.	Elongation per cent. on 4 ins
Copper	Tin.	Phosphorus			
90·93	9·03	0	15·6	5·9	23
90·85	8·92	Trace	16·8	7·2	30
89·18	9·60	0·47	13·6	5·9	6
89·07	9·78	0·91	11·9	5·9	4
88·83	9·18	0·92	11·0	6·5	3·5
88·80	9·32	1·17	11·9	5·5	2·5

From these results it appears that the addition of phosphorus lowers the breaking stress (after a first increase due to the elimination of oxides) and also the elastic limit and the elongation. After an addition of 0·47 per cent., however, the decrease is more gradual It must be noted that the alloys tested by Guillet contain very appreciable quantities of zinc, a metal which should not be present in the best phosphor-bronze.

Phosphor-bronzes containing lead are used for bearings. They will be considered in the chapter dealing with antifriction metals, and it is only necessary to say here that the lead does not alloy with the bronze, but separates in the form of minute globules throughout the metal; while the phosphide of copper separates exactly as in the other bronzes Hence a surface of the alloy contains a number of hard particles (phosphide) and also a number of soft particles (lead), thus fulfilling, as will be seen later, the necessary conditions of a good bearing metal.

The phosphor-bronzes most commonly employed contain (1) 8 to 10 per cent. of tin and 0·5 to 0·7 per cent of phosphorus; (2) 10 to 12 per cent. of tin and 0·7 to 1 per cent. of phosphorus; (3) 10 to 12 per cent. of tin and 1 to 1·5 per cent. of phosphorus.

The first of these is suitable for valves, pinions, pumps, propellers, steam and boiler fittings, etc. It is harder and wears better than gun-metal. The second alloy is considerably harder than the first, and is suitable for worms and worm wheels, valves, pumps, cylinders, motor gearing, etc. The third is an exceptionally hard alloy without being brittle, and is capable of withstanding the hardest wear. It is suitable for worms and worm gearing, slide valves, bearings, and all cases in which the wear is excessive. For castings the Admiralty specify an alloy containing copper 90·0, tin 9·7, and phosphorus 0·3 per cent This is required to give an ultimate tensile strength of 17 tons per sq. in., with an elongation of 15 per cent. on 6 ins., and to withstand bending over a 2-in bar until the two sides are parallel without any sign of cracking.

The following table, giving the results of a large number of mechanical tests on commercial phosphor-bronzes together with their chemical composition, is due to Mr Arnold Philip, the Admiralty chemist. It represents the most complete series of tests yet published, and as it contains a very large amount of useful information in a small space it is reproduced here in full.

[TABLE.

RESULTS OF MECHANICAL AND CHEMICAL TESTS OF PHOSPHOR-BRONZE.

No.	Character of Sample.	Results of Chemical Analysis						Ultimate Tensile Strength in tons per sq. in.	Percentage Elongation on 2 ins.	Percentage Elongation on 6 ins.	Results of Bending Tests.	Remarks
		Copper	Tin	Lead	Zinc	Phosphorus.	Totals.					
1	Casting	82·3	10·8	6·25	nil	0·54	99·89	15·3	12			
2	Bearings	84·5	14·5	nil	,,	0·86	99·86	7·76	1			
3	Casting	85·1	14·3	,,	,,	0·69	100·09	14·56	5			
4	Piston packing ring	85·6	10·8	,,	2·74	0·82	99·96	8·5	3			
5	Casting	86·4	13·0		nil	0·51	99·91	14·55	2			
6	,,	86·6	12·9	,,	,,	0·41	99·91	11·04	5			
7	Gear wheel	85·8	12·2	,,	trace	1·43	99·43	13·4	4·5			
8	,,	87·0	12·0	,,	,,	1·56	100·56	13·94	7			
9	Piston packing ring	87·2	11·2	under 0·3	1·3	nil	99·70	18·5	15			
10	Spanner	87·3	12·2	nil	nil	0·10	99·60	13·69		9·3	Broke when bent 49	Phosphorus too low
11	Sheaves	87·4	11·1	,,	,,	0·49	98·99	18·02	10			
12	Bushes	87·6	11·2	,,	,,	0·53	99·33	20·8	18·75			
13	Sheaves	87·7	10·5	,,	1·39	0·35	99·95	18·96	15			
14	,,	87·8	8·8	3·3	nil	0·33	100·23			5		Rejected on account of lead.
15	Piston packing ring	87·7	10·7	nil	,,	0·97	99·37	23·2	6			
16	Sheaves	88·1	10·5	,,		0·42	99·02	18·23	12			
17	Boat hoist fittings	88·2	10·5	,,	,,	0·51	99·21	17·8		18	Satisfactory	

NOTE.—"Satisfactory," under bending test means that the sample bent without cracking or breaking through 180°.

RESULTS OF MECHANICAL AND CHEMICAL TESTS OF PHOSPHOR-BRONZE—*continued.*

No.	Character of Sample	Results of Chemical Analysis						Ultimate Tensile Strength in tons per sq. in	Percentage Elongation on 2 ins.	Percentage Elongation on 6 ins.	Results of Bending Tests	Remarks.
		Copper.	Tin	Lead.	Zinc.	Phosphorus.	Totals.					
13	Sheaves . .	88·2	8·8	3·2	nil	0·24	100·44	12·7	.	5	.	Rejected on account of lead.
19	,, . .	88·5	10·5	nil	,,	0·56	99·56	15·84		3		...
20	Block . . .	88·4	10·1	,,	1·34	0·16	100·00		...			Complete article tested to 10 cwts.
21	Casting . .	88·2	11·2	,,	nil	0·30	99·70	15·6	12·5	.	...	
22	Worm wheel rim	88·7	10·4	,,	0·58	0·33	100·01	24·2	34·5		..	.
23	Casting	88·9	10·2	,	nil	0·68	99·80	16·4	11			
24	Worm wheel rim	88·8	10·8	,	,,	0·07	99·67	14·8 & 8·66	10 & 3		..	Phosphorus too low. Duplicate mechanical tests made Rejected.
25	Casting . .	88·8	10·3	,,	,,	0·67	99·77	16·4	11		...	
26	Capstan gear	88·9	9·9	,,	0·7	0·40	99·90	15·7	15		Satisfactory	
27	Bearing . .	88·9	10·1	,,	nil	0·82	99·72	13·8	10			
28	Winch casting .	88·8	11·0	,,	,	0·52	100·42	15·5	12			...
29	Bush . . .	88·9	10·3	,,	,,	0·77	99·97	19·0	10·5			
30	Sheaves . .	88·5	10·9	,,	,,	0·20	99·60	18·2	12			
31	,, . .	88·2	10·8	,		0·58	99·58	15·32	.	6·5	..	
32	,, . .	88·4	10·3	,	,,	0·38	99·08	17·5		16·1	..	.
33	,, . .	88·3	10·1	,	,	0·36	98·76	18·0	.	12·3		...
34	Casting . .	89·0	10·2	,,	,,	0·71	99·91	16·4	11			...
35	Spindle . .	89·0	10·1	,,	,,	0·21	99·31	16·28	7·5		...	.
36	Worm wheel rim .	89·1	9·9	,,	,,	0·16	99·16	12·56	...	3·8	.	...

37	Sheaves	89·5	11·3	nil	nil	0·36	101·16	17·91	15·0			The mechanical tests were made in duplicate.
38	Casting	89·4	9·8	,,	,,	0·44	99·64	16·1	9 4			
39	,,	89·8	10·0	,,	,,	0·33	100·13	17·91	16 5			
40	,,	89·8	9·7	,,	,,	0·55	100 05	14·3 & 15·2	6·5 & 7 5			
41	Bearings	89·7	9·4	,,	,,	0·78	99 88	20·2	12			
42	,,	89·2	9·6	,,	,,	0·71	99 51	20·1	15			
43	,,	89·0	10 1	,,	,,	0·58	99 68	26·4	27			
44	Sheaves	89·2	9 9	,,	,,	0·54	99 64	17 3		12 5		
45	,,	89 9	9·5	,,	,,	0·33	99·73	20·8	21		Satisfactory	
46	,,	89·0	10 0	,,	,,	0·50	99 50	14 75		2·25		
47	,,	89 8	9·3	0·27	,,	0·49	99 86	17·5	22		Satisfactory	
48	,,	89 2	10·6	nil	,,	0·42	100·22	18 0	10·4			
49	,,	89 5	10·3	,,	,,	0·32	100·12	18 0	12·5			
50	,,	89·4	10 0	,,	,,	0 57	99·97	17·8		20·8		
51	Worm wheel rim	89 1	10·4	,,	,,	trace	99·40	13 69			Broke when bent through 45°	Phosphorus too low
52	,, ,, ,,	89·4	10 2	,,	,,	trace	99·60	13·69		9·3	..	Phosphorus too low
53	Sheaves	89 4	10·4	,,	,,	0 46	100 26	17·7	11·0			
54	Worm wheel rim	89·7	9·9	,,	,,	0·28	99·88	24 5	54 0		Satisfactory	
55	,, ,, ,,	89 0	10 0	,,	,,	0·35	99·35	25·9	48·0			...
56	Pinion	89·9	8·9	,,	,,	0·54	99 34	18·5	...	22% on 5 ins	Very satisfactory	.
57	Bushes	89·9	9·8	,,	,,	0 65	100 35	21·1	20 0	.		..
58	Casting	89·7	9 9	,,	,,	0 31	99 91	...				
59	Bearing	89·1	10·1	,,	,,	0·72	99·92	18·1	11 0			
60	,,	89·3	10 3	,,	,,	0·38	99·98	16·1				.
61	Worm wheel rim	90·1	9·1	,,	,,	0 34	99 54	21·8		25% on 5 ins.	Satisfactory	
62	,, ,,	90 3	9·0	,,	,,	0·05	99·25				Broke when bent through 49°	Phosphorus too low

RESULTS OF MECHANICAL AND CHEMICAL TESTS OF PHOSPHOR-BRONZE—*continued.*

No	Character of Sample.	Results of Chemical Analysis.						Ultimate Tensile Strength in tons per sq in	Percentage Elongation on 2 ins	Percentage Elongation on 6 ins.	Results of Bending Tests.	Remarks.
		Copper.	Tin.	Lead.	Zinc.	Phosphorus.	Totals.					
63	Worm wheel rim .	90 4	8·6	nil	nil	0 58	99·58	21·1		20% on 5 ins	Very satisfactory	
64	,, ,, ,,	90·9	8·8	,,	,	0·16	99·86	15·8	27·5			Phosphorus too low
65	,, , ,,	90 0	9·3	,,	,	0·30	99·60	20·4	20 0		Bar broke at 90°	
66	,, ,, ,,	90·4	9·3	,,	,,	0·46	100·16	27 5	53 0			
67	Stuffing box . .	90·4	9 6	,,	,	0 34	100·34	18·6	21·1		...	
68	Sheaves . .	90·4	8 9	,,	,,	0·73	100 03	18 5 & 20	24 & 26			The mechanical tests were made in duplicate.
69	,, . .	90·2	9 6	,,	,,	0·22	100·02	17 8 & 16·3	7·8		..	,,
70	,, . .	90·4	9·2	0·1	,,	0·45	99·95	22·9	31·2			..
71	Gear wheel . .	90 5	9·5	nil	,,	0·08	100 08	23 8	54 0			
72	Casting . .	90·0	9·6	,,	,,	0·42	100 02	13 0	7 5			..
73	Sheaves .	90·3	9·7	,,	..	0·15	100·15	16·8 & 17·5		22·9 & 21 5	Satisfactory	The mechanical tests were made in duplicate
74	Bearing .	90 6	8·4	,,	,,	0·53	99·53	21·0	28		Satisfactory	...
75	,, . .	90·9	8·4	..	,,	0 37	99·67	19 2	21	...	,,	
76	,, . .	90·5	8 9	,,	,,	0 42	99·82	20·3	20			.
77	Sheaves . .	90·4	8·7	0·18	,,	0 53	99·81	17·5	22		Satisfactory	..
78	Bush . . .	90·9	8·3	nil	,,	0·46	99 66	20·1	30	..	,,	...

79	Sheaves	91·3	8·5	nil	nil	0·37	100·17	18·4	...	16	Bent 90° did not break	
80	Bush	91·3	8·2	,,	,,	0·45	99·95	20·1	30		Satisfactory	...
81	Spindle	91·3	9·0	,,	,,	0·29	100·59	16·9 & 18·8	16 & 25	...		...
82	Sheaves	92·3	7·2	,,	,,	0·42	99·92	24·3	50			
83	Elec motor fittings	93·9	5·6	,,	,,	0·58	100·08	22·4	18·5		Satisfactory	
84	Bushes	94·4	5·2	,,	,,	0·45	100·05	16·6	20·0			
85	Worm wheel rim	94·2	4·9	,,	,,	0·96	100·06	25·0	28·0		Satisfactory	
86	,, ,, ,,	94·4	4·8	,,	,,	0·98	100·18	24·8	36·0		,,	
87	Rod	94·5	5·2	,,	,,	0·20	100·20	21·75	39·0		,,	
88	Worm wheel rim	95·5	4·9	,,	,,	0·95	101·35	24·6	34·0		,,	
89	,, ,, ,,	95·2	3·8	,,	,,	0·86	99·86	22·9	43·0		,,	
90	Rolled plate	95·4	4·0	,,	,,	0·21	99·61	31·35		5·0		Reduction of area 46·5%.
91	,, ,,	95·2	4·0	,,	,,	0·21	99·41	22·4	...	33·3		
92	Rolled sheet	96·2	4·1	,,	,,	0·23	100·53	33·85	17			
93	Rod	96·1	3·8	,,	,,	0·11	100·01	42·94	17			Reduction of area 67%.
94	,,	96·5	3·4	,,	,,	0·11	100·01	42·6	10	...		
95	,,	96·9	2·9	,,	,,	0·11	99·91	46·04	11	6·7		Reduction of area 46%.
96	Rolled sheet	96·9	3·0	,,	,,	0·13	100·03	29·8	18			,, 63·8%.
97	Rod	97·1	2·2	,,	,,	0·40	99·70	19·7	58			,, 84·5%.
98	Rivets	99·2	0·8	,,	,,	nil	100·00	18·8	42		Satisfactory	,, 91·8%.
99	,,	99·2	0·8	,,	,,	,,	100·00	18·8	42	...	,,	,, 91·8%.

Most of these alloys may be described as true phosphor-bronzes; but there are many others that contain, at the most, traces of phosphorus, and it is probable that at the present time very little bronze of any description is made without the addition of a small quantity of phosphorus as a deoxidiser.

Manganese-bronze.

As in the case of phosphor-bronze, the term "manganese-bronze" is applied to alloys of very variable composition. It may be stated at the outset, however, that in the great majority of cases the expression is somewhat misleading, as the alloys differ very slightly in composition from the ordinary brasses. It is only in rare cases that a copper-tin alloy containing manganese is met with. These usually contain from 1 to 3 per cent. of manganese, which is often accompanied by 4 or 5 per cent. of zinc and some lead. Guillet cites two cases of alloys employed for hydraulic machinery at high pressures having the following composition:—

	I	II.
Copper	82·0	83·5
Tin	8·0	8·0
Zinc	5·0	5·0
Lead	3·0	3·0
Manganese	2 0	0·5

Although such alloys are seldom used they are not without interest, and a passing reference may be made to the influence of manganese on the copper-tin alloys Guillet has submitted a series of alloys, containing manganese in varying amounts, to mechanical tests, with the results shown in the table:—

Composition.			Tensile Strength. Tons per sq. in.	Elastic Limit Tons per sq. in.	Elongation per cent. on 4 ins.
Copper.	Tin.	Manganese.			
90·93	8·82	0	15·6	5·9	23
90·12	9·20	Traces	17·1	5·7	28
87·64	10·41	1·67	13·6	6 4	20
89·38	8·61	0 69	10·4	6 2	7·5
85·87	8·76	3·10	7·5	7·5	0

From these results it would appear that the first effect of manganese (probably due to its influence as a deoxidiser, much in the same way as phosphorus) is to give a higher breaking stress and elongation. When present to the extent of more than traces, however, the alloy rapidly becomes brittle, unless zinc is present at the same time.

The addition of manganese to copper alloys was attempted by Stirling, Parkes, and others; but their efforts met with little success until, in 1876, Parsons was granted a patent (No. 842) for the addition of manganese in the form of ferro-manganese to copper-tin or copper-zinc alloys These alloys were stronger than simple bronzes or brasses, but difficulties were experienced in obtaining sound castings. These were overcome by the addition of aluminium, and a second patent was granted in 1888 (No. 11512) to cover this improvement. It was then found that the addition of these metals to brass gave results so much superior to those with bronze that the copper-tin alloys were practically abandoned. The name, however, was never dropped, and, as already mentioned, the alloys to this day are invariably described as manganese-bronzes. Many of the best modern manganese bronzes differ but little from Parsons early bronzes, as will be seen from the following analyses of two samples, one made in 1893 and the other in 1913:—

	Parsons Bronze. 1893.	Modern Bronze. 1913
Copper	56·48	54·94
Tin	1·15	1·36
Iron	1·20	1·16
Aluminium	0·20	0·35
Manganese	0·11	0·47
Zinc	40·84	41·66

Putting aside the copper-tin alloys containing manganese, the alloys sold commercially as manganese-bronzes may be divided into two classes:—

1. Alloys of copper and manganese containing about 4 to 6 per cent. of manganese.

2. Alloys of copper and zinc to which ferro-manganese or cupro-manganese containing iron has been added. These alloys frequently contain aluminium and sometimes tin, but the principal constituents are copper and zinc.

The alloys belonging to the first class have a somewhat limited application, their principal feature being their strength at high temperatures. For this reason they have been very largely adopted, more especially on the Continent, for firebox stays.

The addition of manganese to copper does not materially harden the copper, but raises the tensile strength. The following figures are the results obtained by Guillet for small additions of manganese.—

Cu.	Mn.	Tensile Strength. Tons per sq. in.	Elastic Limit. Tons per sq. in	Elongation per cent. on 4 ins.
96·95	2·94	14·0	6·3	45
95·40	4·10	15·2	7·3	42
93·38	6·56	17·4	8·4	33·5

The complete series of copper manganese alloys has not received much attention, but the alloys used commercially are solid solutions of manganese in copper. Photograph 20 shows a section of a firebox stay containing 96 per cent. of copper and 4 per cent. of manganese With less than 9 per cent. of manganese the alloys can be rolled or drawn.

The use of these alloys for firebox stays will be considered in the chapter dealing with the behaviour of alloys at high temperatures

The alloys of the second class are those most commonly met with under the name of manganese-bronzes, although they would be more accurately described as manganese-brasses. From a theoretical point of view they have been little studied, but it is evident from the number of constituents present that their constitution must be of a complex character. Many manganese-bronzes contain only traces of manganese, and some fail to show even traces on analysis. In these the manganese has probably served its purpose purely as a deoxidiser, but it has left behind it the iron with which it was associated, and the influence of this metal must be considered, as it occurs in by no means inappreciable quantities in nearly all these alloys. The addition of manganese alone (that is to say, without the simultaneous addition of iron) to the copper-zinc alloys has the effect of increasing the tensile strength and the elastic limit with a decrease in the elongation. The alloys also become harder and more brittle. As regards their constitution the manganese enters into solution, with the result that the microstructure is the same as that of the copper-zinc alloys. This probably accounts for the statement made by Guillet that the microstructure of manganese brasses is the same as that of copper-zinc alloys; but the commercial varieties of these alloys invariably contain iron, usually in very much larger quantities than the manganese, and their structure is very different from that of the ordinary brasses. Photographs 21 and 22 show the structure of a forged manganese bronze containing 58·6 per cent. copper, 38·4 per cent. zinc, 1·6 per cent. iron, and 0·02 per cent. manganese. Manganese bronzes containing upwards of 60 per cent. of copper are suitable for forging and rolling, while those containing less than 60 per cent. of copper are used for castings; and both of these varieties are made in various qualities according to the purposes for which they are required. Manganese-bronzes suitable for forging or rolling, such as those manufactured by the Manganese Bronze and Brass Company, have an ultimate strength ranging from 27 tons in the mild quality to 38 tons in the high quality, the elastic limit ranging from 10 to 20 tons, and the elongation from 20 to 15 per cent. If the metal is cold-rolled the ultimate strength can be obtained as high as 40 to 50 tons per sq. in.

Bronzes of this description are used for studs, bolts and nuts, pump-rods, pins, keys, etc., and, in fact, for practically all purposes for which yellow brass or Muntz metal are used. It can also be drawn into tubes which can be easily bent, either hot or cold, and are much stronger than brass or copper tubes. On this account, together with its freedom from corrosion, it is largely used for hydraulic tubes under heavy pressure.

In the form of plates and sheets it is of value in cases where a metal is required to withstand corrosion, such as strainer plates, sheathing for yachts, pump valves, etc.

Cast manganese-bronze, like the rolled variety, is made in different qualities according to requirements, and has an ultimate tensile strength of from 32 to 38 tons per sq. in., with an elastic limit varying from about 15 to 19 tons per sq. in., and an elongation of about 15 to 30 per cent. on 2 ins.

It is exceedingly tough, and is used for parts of marine engines, hydraulic rams, valves and cylinders, etc. Probably its most important application is in the manufacture of propellers and propeller blades. As compared with iron or steel propellers, it has many advantages. It is lighter, and therefore the strains on the shafting, bearings, etc., are considerably reduced. Further, it is practically unaffected by sea water, so that the propeller blades retain their smooth surface. In the case of iron and steel the pitting due to the corrosion of the sea water causes a falling-off in the speed, and in time necessitates the renewal of the propeller. It has been stated that the substitution of a manganese-bronze propeller in place of an iron one increases the speed of a vessel by about half a knot for the same coal consumption. Moreover, the alloy is capable of being worked cold, and in several cases where the propeller blades have been injured by accidents they have been hammered into shape without any sign of breaking.

A minor, but not altogether unimportant, consideration is the fact that a bronze propeller is always of value as a copper alloy. These advantages more than compensate for the extra initial cost of a manganese-bronze propeller

In the early days of manganese-bronze propellers erosion was a serious source of trouble, but it is claimed that the addition of about 2 per cent. of nickel to the alloy renders it immune from this trouble.

The addition of aluminium to manganese-bronze gives rise to a series of alloys possessing very remarkable and useful properties. Bronzes of this description were placed upon the market several years ago under the name of "Immadium" by the Manganese Bronze and Brass Company. They have an ultimate tensile strength of 38 tons per sq. in. in the case of forgings, and 42 tons per sq. in. in the case of rolled rods, with an elongation of from 20 to 25 per cent., and are made of different qualities to suit requirements. The structure of these alloys is very similar to that of ordinary manganese-bronze, but of somewhat finer and closer grain, the aluminium appearing to enter the alloy in the form of a solid solution. Photographs 23, 24, 25, and 26 show the structure of two samples of Immadium-bronze. The alloys work perfectly and take a very fine polish. They may be used for all purposes where strength and toughness are required, but their most valuable property is the remarkable resistance to the action of corrosive liquids which they possess. On this account they have been largely used in the manufacture of rods, valves, and other parts of pumps having to deal with acid water.

Aluminium-bronze.

The term "aluminium-bronze" is applied to alloys of copper and aluminium containing from 2 to 10 per cent. of aluminium. With more than 10 per cent. the alloys rapidly become brittle, and beyond 11 per cent. they are valueless from an industrial point of view.

The first aluminium-bronze was made by Dr Percy, and its properties studied by Debray, but at that time aluminium was a rare and expensive metal, so that for many years the alloy, which was known as "aluminium gold," was regarded rather as a curiosity than a commercially useful alloy. With the introduction of electrical methods of reducing aluminium, however, aluminium bronze became a practical alloy, and was placed on the market by the Cowles Smelting Company, who manufactured alloys containing from 1¼ to 11 per cent. of aluminium, for which they claimed an ultimate tensile strength ranging from 9 tons per sq. in. in the 1¼ per cent. alloy to 50 tons per sq. in. in the 11 per cent. alloy. Since then the manufacture of aluminium has been much improved and the price lowered, but it is still sufficiently high to prevent the alloys being more extensively used.

The properties of the copper-aluminium alloys have been studied by Gautier, Le Chatelier, and Guillet, and, more recently, by Carpenter and Edwards, who have confirmed and extended the work of Guillet. The equilibrium diagram of the series is shown in fig. 56, but, as already mentioned, we are only concerned with a small portion of the curve, viz. that of the alloys containing less than 11 per cent. of aluminium, as the other alloys (with the exception of a few represented by a small part of the curve at the other end, which will be considered later) are of no industrial importance. As regards the alloys lying between these two portions of the curve there is a definite compound corresponding to the formula $CuAl_2$, which forms a simple series of alloys with aluminium, having a eutectic containing 67 per cent. of aluminium. There is little doubt that a compound corresponding to the formula Cu$_3$Al exists, and, possibly, one corresponding to Cu$_4$Al; but these compounds do not form simple alloys with copper. They give rise to a series of solid solutions of a complex and unstable character.

Aluminium-bronzes may be conveniently divided into two groups, viz.—(1) those containing from 0 to 7·35 per cent. of aluminium; and (2) those containing from 7·35 to 10 per cent. Up to 7·35 per cent. the alloys consist of a single homogeneous solid solution and are extremely ductile (photographs 28 to 31), whereas the alloys containing more than 7·35 per cent. contain a hard, dark-coloured constituent which is accompanied by an increase in the tensile strength of the alloys and a decrease in ductility. The curves in figs 57, 58, and 59 are plotted from the results obtained by Carpenter and Edwards on sand castings, rolled bars, and cold-drawn bars respectively; and are quite in accordance with what would be expected from the microscopical appearance of the alloys.

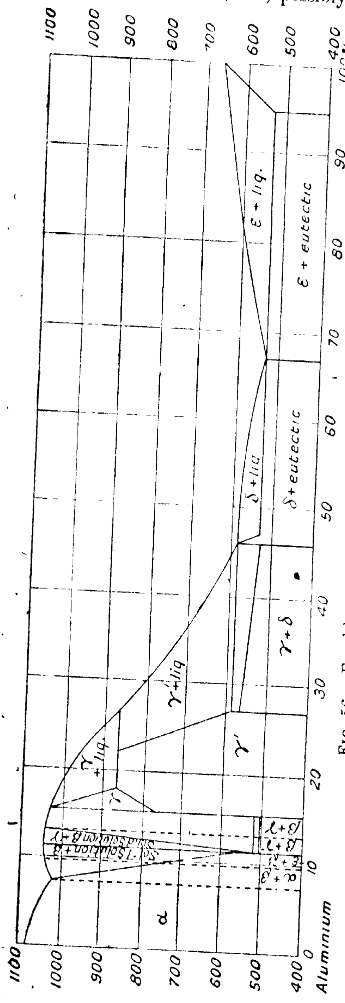

FIG. 56.—Equilibrium Diagram of Copper-Aluminium Alloys.

The bronzes belonging to the first group (*i.e.* those containing less than 7·35 per cent. of aluminium) are very similar to high grade brasses containing 70 per cent. of copper, and can be employed for many purposes in place of brass. The alloys can be readily forged and rolled, and can be drawn cold. Unfortunately, their high price is a serious drawback to their more extended use, except in special cases; but the alloys containing 2 per cent. of aluminium have been used in the manufacture of tubes and those containing 5 per cent. for rods, etc., while, owing to their beautiful gold colour, they have been largely used for art castings and cheap jewellery.

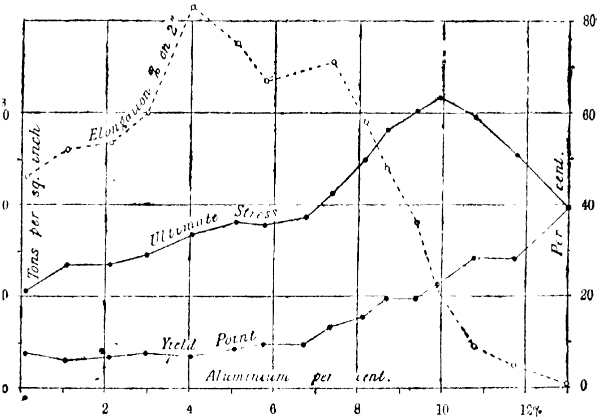

FIG. 57. Tensile Tests on Sand Castings.

Many of the difficulties met with in brass, such as "season cracking," are also common to aluminium-bronze, and it has been found that tubes which have received too great a pinch in the drawing will fracture in the course of a few months in exactly the same way as brass tubes. Moreover, on annealing aluminium-bronze the crystals increase in size, just as in the case of brass. This growth of crystal is accompanied by a decrease in the ultimate strength of the alloy and a very marked falling-off in the yield-point. The table on p. 209 gives the results obtained by Carpenter and Edwards in the case of four alloys

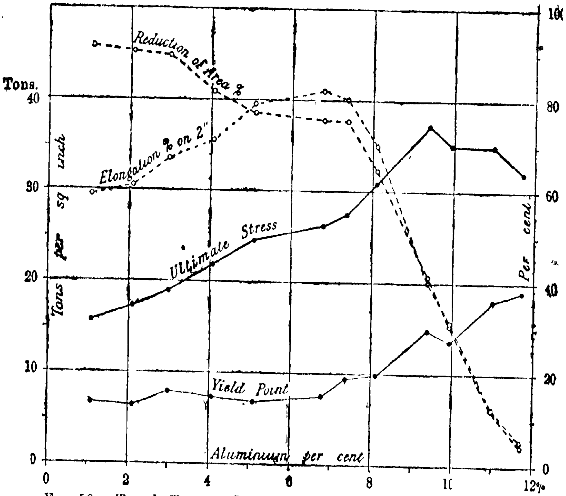

FIG. 58.—Tensile Tests on Bars rolled to 1¼ in. diameter (untreated).

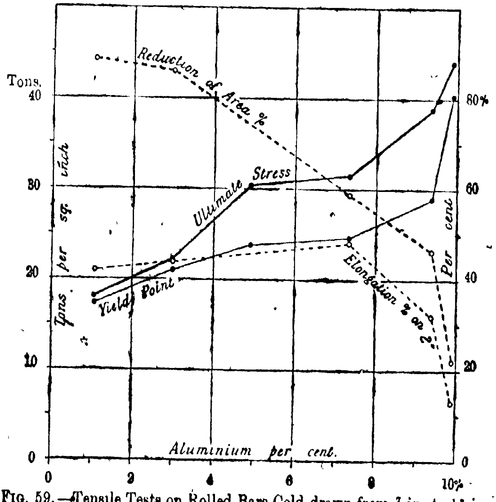

FIG. 59.—Tensile Tests on Rolled Bars Cold-drawn from ⅞ in. to $\frac{13}{16}$ in.

Aluminium.	Condition.	Yield-point.	Ultimate Stress.	Elastic Ratio.	Elongation on 2 in.	Reduction of Area.
Per cent.		Tons per sq. in.	Tons per sq. in.		Per cent.	Per cent.
	Rolled—					
0·10	Untreated	6·9	14·50	0·48	65·5	90·71
	One hour at 600° C.	5·0	14·11	0·35	65·0	91·60
	,, 900° C.	5·8	13·26	0·44	56·0	87·65
2·99	Untreated	11·6	19·79	0·59	57·25	86·11
	One hour at 600° C.	6·9	18·54	0·37	66·00	89·84
	,, 900° C.	5·8	19·76	0·30	82·5	83·60
5·76	Untreated	11·8	28·40	0·42	74·2	76·93
	One hour at 600° C.	9·4	27·20	0·33	77·0	75·00
	,, 900° C.	6·0	23·65	0·25	86·0	70·00
7·35	Untreated	10·6	29·68	0·36	72·5	74·34
	One hour at 900° C.	7·1	23·89	0·30	92·0	72·00

In these experiments the alloys were only heated for one hour; but a practical example of the effects of continued heating has been recorded in the case of a locomotive belonging to the London and North-Western Railway Company, which was fitted with aluminium-bronze firebox stays. After being in use for two months, during which time the locomotive had run only 2400 miles, it had to be taken off the road on account of the number of fractured stays. This question of the mechanical properties of alloys at temperatures above the normal is an exceedingly interesting one, and is dealt with in more detail in another chapter.

As regards the general heat treatment of these alloys their properties appear to be little affected, whether slowly cooled or quenched. In this respect they differ from the alloys of the second group, containing more than 7·35 per cent. of aluminium. The curves in figs. 60, 61, and 62 show the results obtained by Carpenter and Edwards on chill castings and on sand castings slowly cooled and quenched from 800° C.

The alloys belonging to the second group are composed of two constituents, the new component being a hard acicular mass, which was formerly supposed to be a eutectic (photograph 32); but when examined under high powers its structure can be easily distinguished from that of a eutectic. Photograph 33 shows the striated or acicular structure of this constituent. It appears to be a solution of an unstable character, as it is profoundly altered by heat treatment. Under prolonged annealing it gradually loses its structure and appears to reach a stable condition. Consequently, the alloys containing the constituent are considerably altered by thermal treatment as shown in the curves. The

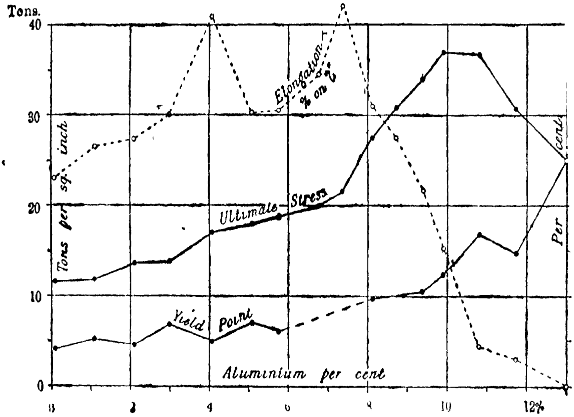

FIG. 60.—Tensile Tests on Chill Castings

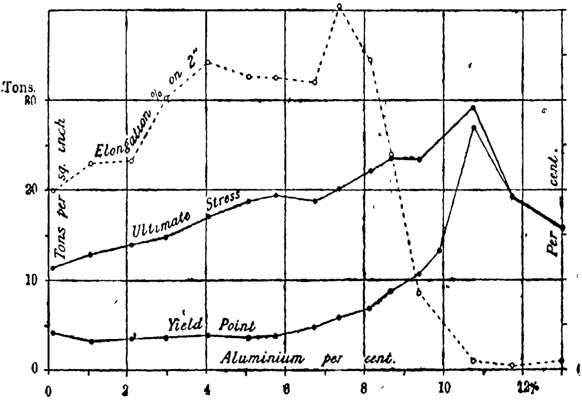

FIG. 61.—Tensile Tests on Sand Castings slowly cooled from 800° C.

bronzes of this class are still ductile, and have been used for propellers, while Carpenter and Edwards claim that they are unsurpassed for the production of castings intended to withstand high pressure.

Fig. 63 gives the curve representing the hardness of the series of alloys containing aluminium up to 15 per cent., as determined by the Brinell test, and illustrates very plainly the rapid increase in hardness caused by the appearance of the hard constituent.

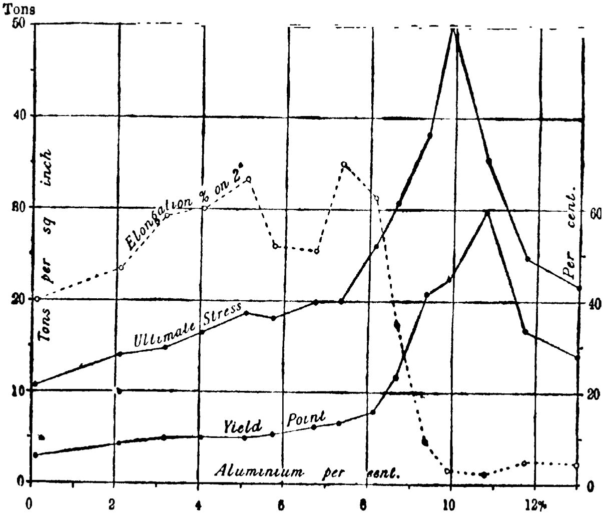

FIG. 62.—Tensile Tests on Sand Castings, quenched from 800° C. in Water.

The melting and casting of aluminium-bronze present no great difficulty, although both operations must be carried out with greater care than is necessary in the case of ordinary bronze or brass owing to the readiness with which the aluminium becomes oxidised. The alloys are melted in graphite crucibles under a layer of charcoal and with as little stirring as possible to prevent oxidation. Under these conditions very little alteration in composition is noticeable on remelting. The fact recorded by several observers that copper and aluminium unite with the production of intense heat is due, not so much to the combination of copper and aluminium, as to the combination of the oxygen contained in the copper with the aluminium. The heat evolved on alloying deoxidised copper with aluminium is comparatively slight.

Aluminium-bronze undergoes considerable contraction on cooling, and allowance must be made for this in casting the alloys, by providing large gates and a good head of the molten metal. The casting should also be carried out at as low a temperature as possible. There is no doubt that the contraction or shrinkage of aluminium-bronze, together with its proneness to oxidation, have done much to hinder its adoption for many purposes for which it might be usefully employed. The large risers required to com-

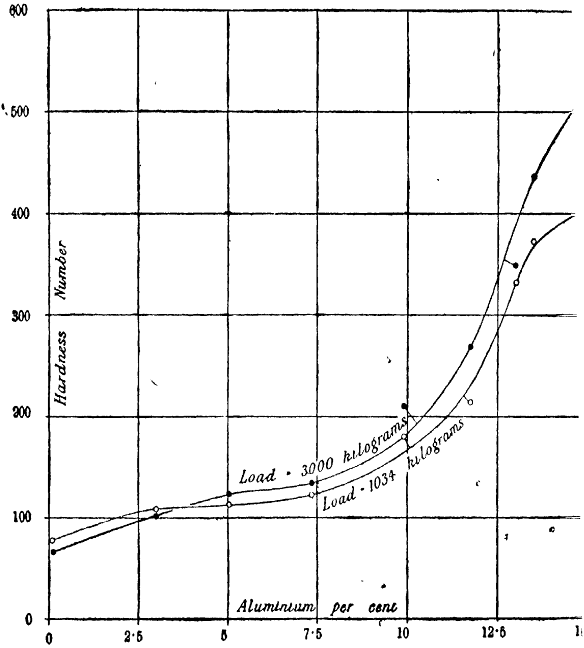

FIG. 63.—Hardness Number $\frac{\text{Load (kilograms)}}{\text{Superficies of Concavity } (mm^2)} \times \sqrt[5]{p}$ (where p = Radius of Hardened Ball).

pensate for the shrinkage necessitate the melting of an excess of metal and the production of large quantities of scrap to be remelted, thereby raising the cost of production.

As regards the almost instantaneous oxidation of the surface of the molten alloy when exposed to the air, and the difficulty of keeping this oxide out of the castings, Sperry says: "The greatest obstacle in the way of casting aluminium-bronze is its oxidation when melted. Whenever the surface of the molten metal is exposed to the air, a film of oxide of aluminium forms on it. The more it is exposed, the greater the amount. This explains why such a large amount of dross forms when aluminium-bronze is being stirred. When allowed to remain at rest in a crucible, very little forms, as the surface of the metal is protected by the film already on it. It also shows why aluminium-bronze should always be poured with as little stirring as possible. Any agent, such as wet sand, which tends to stir the metal up, produces dross and the accompanying dirty castings. The more quietly aluminium-bronze can be poured, the better the castings. The only method," he adds, "by which it can be cast in a commercial manner is to prevent its being agitated while the pouring is taking place, either by stirring, too high a drop from the crucible to the mould, or by wet sand. The more quietly it can be poured, the smaller the quantity of dross. Dross which forms in melting may be skimmed off, but that which forms while the pouring is taking place enters the casting. The various skim gates, pouring from the bottom, etc., are all efficacious, as they serve to trap the dross and prevent its entrance into the casting."

In addition to the binary alloys of copper and aluminium, alloys containing a small percentage of nickel have been placed on the market. The addition of nickel appears to give harder and stronger alloys, but there is very little available information as to their practical uses.

Aluminium-bronzes containing 1 to 2 per cent. of silicon have also been placed on the market under various trade names. The addition of silicon has the effect of increasing the tensile strength of the alloy, while the falling-off in the elongation appears to be very considerable.

Aluminium-brass.

Aluminium-brass, as its name implies, is a brass containing a small quantity—not exceeding 4 per cent.—of aluminium. The alloys were placed on the market by the Cowles Electric Smelting Company, together with an alloy containing iron in addition to aluminium, which was known as **Hercules metal.** These alloys are still in use, and reference has already been made to manganese-brasses containing aluminium.

The constitution of aluminium-brasses has been studied by Guillet, and his results are of considerable interest. His experiments have been carried out on the two important types of brass containing respectively 30 and 40 per cent. of zinc by adding increasing quantities of aluminium. He finds that the structure of the alloys is the same as that of the common brasses, the aluminium appearing to have the same effect as zinc, but to a greater degree. Thus an alloy containing 38 per cent. of zinc and 2 per cent. of aluminium has the structure of a brass containing 45 per cent. of zinc; and this holds good with all the alloys, so that Guillet argues that in these alloys 1 per cent. of aluminium is equivalent to 3½ per cent. of zinc.

With more than 4 per cent. of aluminium the alloys are difficult to work.

Aluminium-brass gives excellent castings, and can be rolled and forged while hot. It is suitable for pumps, valves, pinions, etc., and also for propellers. Guillet states that the alloys have been used in France for the construction of submarines, but that they have not proved entirely satisfactory.

The mechanical properties of several of the alloys have also been determined by Guillet, and his results are shown in the table (see p. 215).

A number of aluminium-brasses, to some of which a small percentage of iron has been added, are now on the market, and their properties are similar to those of the manganese brasses to which reference has already been made. The addition of iron is of interest, as it alters the structure and properties of the alloys to some extent. The iron unites with a portion of the zinc to form a definite compound which separates out as small particles or crystals, thus forming a nucleus around which the so-called δ

constituent solidifies. This structure, which is illustrated in photograph 26, confers upon the alloy the power of increased resistance to wear without materially affecting its strength or ductility.

Composition.			Tensile Strength in tons per sq. in.	Elastic Limit in tons per sq. in	Elongation per cent.
Copper	Zinc.	Aluminium.			
70 0	29 6	0 0	8·7	3 6	50
69·0	29 9	0 1	12·6	2·9	59
70 0	28·8	0 9	14 4	4·2	67
70·5	26·4	3 1	21·5	8 5	50
70·1	24·7	5 2	32·2	4 7	11
60 0	40·0	0 0	20·2	5 1	47
59 6	40·1	0 3	20·5	6·2	51
59 9	40·3	0·8	19 6	6 0	45
59 6	38 5	2 9	29 2	7 5	14
60 4	35·9	4·7	28·0	11·3	2

MECHANICAL TESTS ON ALLOYS, ROLLED, DRAWN AND ANNEALED.

Composition.			Tensile Strength in tons per sq. in.	Elastic Limit in tons per sq. in.	Elongation per cent.
Copper.	Zinc.	Aluminium.			
61·4	38 4	0·7	22·3	6·4	45
60 3	38·2	1·1	24·2	7·1	36
61·0	37·7	1·4	23·3	7·8	43
59 9	37·9	2·0	24·8	11·5	17
59·8	37·2	2 7	28·2	11·2	16
60 0	36·4	3 9	30·5	11·6	13

Vanadium-Bronze.

Although vanadium-bronze has made little progress in this country it appears to have met with greater success in America, where it is said to be largely used by the U.S. Government for naval construction, as well as by private founders.

The effect of vanadium upon copper and its alloys appears to be, like many other deoxidisers, twofold. In the first place, it removes all oxides, thereby giving sounder castings and more homogeneous metal. A small addition of vanadium enables pure copper to be cast with ease, and the ductility is rather increased than decreased. The possibility of making intricate castings of pure copper is of the greatest importance in the electrical industry, and vanadium is of great assistance in this respect, but it must be remembered that an excess of vanadium increases the electrical resistance of the copper to a serious extent. For other than electrical purposes, however, an excess of vanadium increases the strength of copper and copper alloys. Some results obtained on these alloys in America have been given by Norris. He states that tests on a 60/40 brass in which only a trace of vanadium remained showed an increase in tensile strength from 17 to 22 tons per sq. in. and an increased elongation on 2 ins. from 28 to 45 per cent. Tests on two samples of manganese-bronze are also given as follows:—

Composition.		
	Manganese-Bronze.	Manganese-Vanadium-Bronze.
Copper	58·81	58·56
Zinc	38·08	38·54
Aluminium	1·22	1·48
Manganese	0·69	0·48
Iron	0·84	1·00
Vanadium	nil	0·03
Tests.		
Ultimate tensile strength	24·2 tons	36·4 tons
Elastic limit	13·6 ,,	22·6 ,,
Elongation on 2 ins.	22 per cent.	12 per cent.
Reduction of area	18 ,,	14 ,,

An alloy similar to manganese-bronze but in which the manganese is replaced by vanadium is said to be largely used in marine work, and the following tests are given for the cast and cold drawn metal:—

	Cast.	Cold Drawn.	
		⅝-inch rod.	⅜-inch wire.
Ultimate tensile strength	31·7 tons	41·1 tons	45 0 tons
Elastic limit . . .	12·1 ,,	35·7 ,,	36·4 ,,
Elongation on 2 ins. .	32 per cent.	11 5 per cent.	12·0 per cent.
Reduction of area . .	27·8 ,,	29·3 ,,	33·6 ,,

Experience in this country is insufficient to enable any definite conclusion to be arrived at with regard to the merit of vanadium as compared with other metals commonly used as additions to copper alloys.

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CHAPTER X.

GERMAN SILVER, AND MISCELLANEOUS COPPER ALLOYS.

GERMAN silver probably exists under a greater number of names than any other alloy. Nickel silver, argentan, packfong, white copper, silveroid, silverite, Nevada silver, Potosi silver, Virginia silver, and electrum are some of the names which have been used to describe it in this country; while on the Continent it is known as *maillechort* (after Maillet, who introduced it into France in 1719), *alfénide argyroide*, *neu-silver*, and *weiss-kupfer*. The alloy consists of copper, nickel, and zinc, but the quantities vary considerably in different samples. Before dealing with the ternary alloy it may be well to briefly consider the binary alloys of copper and nickel, as they have (to a limited extent) their own industrial applications. Unfortunately, very little work appears to have been done in connection with either series of alloys, and the information concerning them is incomplete and unsatisfactory.

From the freezing-point curve of the copper-nickel series, as determined by Gautier, it would seem that a compound corresponding to the formula CuNi is formed, which is soluble in copper and nickel. The micro-structure of the alloys confirms the view that they are solid solutions, but does not indicate the existence of a compound. The electrical conductivity of the series, however, shows a minimum in the alloy containing 40 per cent. of nickel, which is not far removed from the composition of the supposed compound; but, on the other hand, the measurement of the electromotive force of the alloys fails to indicate the existence of a compound.

Apart from the alloy containing 50 per cent. of nickel, which is used in the manufacture of German silver, the alloys generally used contain quantities of nickel not exceeding 25 per cent. These alloys, when cast, exhibit the characteristic structure of quickly-cooled solid solutions, but, on annealing, the crystallites undergo gradual absorption and are replaced by the regular crystalline structure of simple metals and homogeneous solid solutions. This change of structure with annealing has been considered in some detail in the case of the copper-zinc alloys containing 30 per cent. of zinc.

An alloy containing 25 per cent. of nickel has been largely used as a coinage alloy, but at the present time there appears to be a tendency to substitute nickel coins for those of the alloy. A 25 per cent. alloy has also been used for locomotive firebox plates with satisfactory results; while an alloy containing only 5 per cent. of nickel has been adopted by the British Government for the driving bands of projectiles. Copper containing 3 per cent. of nickel has also been found to give excellent results for locomotive boiler tubes. In this connection an instructive experiment was made by Mr Webb of the London and North-Western Railway Works at Crewe. A four-wheels-coupled passenger engine was fitted with 198 tubes by ten different makers and a record kept of the tubes requiring renewal. The first tube failed after the engine had run 34,067 miles, and the second tube (of the same make) after 40,612 miles. The first and only failure of the make which stood best did not occur until the engine had run 123,896 miles. The failure of the tubes, which was due to wear from the inside by the corrosion of furnace gases and abrasion of cinders, invariably occurred at a point within 6 ins. of the firebox and at the bottom of the tube. Analyses of all the tubes showed that those giving the best service contained about 3 per cent. of nickel, and excellent results were obtained from those containing not less than 0 5 per cent. of arsenic. The use of alloys containing about 2 per cent. of nickel for firebox stays has already been mentioned.

An alloy containing 60 per cent. of copper and 40 per cent. of nickel is known under the name of constantan, and is used in the form of wire for electric resistances, and also in conjunction with a copper wire as a thermoelectric junction suitable for the measurement of temperatures which are not sufficiently high to necessitate the use of a platinum couple.

During the last few years an alloy of nickel and copper to which the name Monel metal has been given has been very largely used in America. It is produced by the direct reduction of the nickel-copper matte obtained by smelting the mixed sulphide ores of these metals as they occur in Ontario. Naturally the composition varies within certain limits, and additions may also be made in order to alter the mechanical properties to suit requirements. The composition of the natural alloy is approximately 6·7 per cent. nickel, 28 per cent. copper, 2 to 3 per cent. iron, together with small quantities of silicon, manganese, etc. A sample of rolled metal of this composition gave a tensile strength of 47 tons per sq. in., with an elastic limit of 34 tons, and 20 per cent. elongation on 2 ins.

The alloy casts well if a suitable deoxidiser such as aluminium or magnesium is used, and it is capable of being rolled into rods, sheets, etc., without difficulty. It resists corrosion remarkably well, and is being used in America for the manufacture of propellers. The U.S. Government specification for the composition of the alloy for this purpose is:—

Nickel	60·0	per cent.
Copper	33·0	,,
Iron	6·5	,,
Aluminium	0·5	,,
Lead	nil	

This gives a tensile strength of 37 tons, with an elastic limit of 17 tons, and an elongation of 44 per cent. on the cast alloy, and 39 tons tensile, 26 tons elastic limit, and 40 per cent. elongation on the rolled metal. Other physical properties given for this alloy as cast are, specific gravity 8·87, melting-point 1360°, hardness (scleroscope) 22, electrical conductivity 4 (taking copper as 100), and shrinkage ¼ in per foot. Monel metal is said to have been used in Germany for firebox plates, but information on this point is lacking.

Owing to the remarkable resistance to corrosion shown by the nickel-copper alloys containing high percentages of nickel, attempts have naturally been made to adapt these alloys to various engineering purposes. If, for example, part of the nickel in an alloy similar to Monel metal is replaced by tin, the ductility of the alloy is lowered, but it possesses great resistance to corrosion, a low coefficient of friction, and is unaffected by moderately high temperatures. It is therefore a valuable alloy for the construction of such parts as the seats and discs of high-pressure steam valves. An alloy for this purpose containing approximately 54 per cent. of nickel, 33 per cent. of copper, and 13 per cent. of tin, known as Platnam metal, is due to the enterprise of Messrs J. Hopkinson & Company, who were the first to realise the importance of these alloys.

The addition of zinc to the copper-nickel alloys is not attended with the formation of compounds, and the resulting alloys (the German silvers) consist of a single homogeneous solid solution. Photograph 34 shows the structure of a rolled German silver. They may be regarded either as brasses containing nickel in solution, or as copper-nickel alloys containing zinc in solution. They are very ductile, and can be rolled, hammered, stamped, and drawn. At the same time they are hard, tough, not easily corroded, and, above all, possess the valuable property of being white. As in the case of most solid solutions, the alloys are softened by annealing.

The following table gives the results of a number of analyses of German silvers (collected by Hiorns) with the names of the authorities :—

Authority.	Composition per cent.					
	Copper	Nickel.	Cobalt.	Zinc.	Iron.	Lead.
1. Fyle	40·4	31·6	…	25·4	2·6	…
2. Fricke	50·0	31·2	…	18·8	…	…
3. Guettier	53·3	26·6	…	20·1		…
4. ,,	51·6	26·0	…	22·4	…	…
5. Krupp	51·6	25·8	…	22·6	…	…
6. ,,	48·5	24·3	…	24·3	…	2·9
7. Hiorns	57·0	24·3	…	18·7	…	
8. Guettier	59·0	22·2	…	18·5	…	0·3
9. ,,	55·2	21·4	…	23·4	…	
10. Hiorns	59·1	20·2	…	20·4	0·3	…
11. ,,	56·5	20·3	…	23·2		…
12. Henry	67·0	19·3	…	13·6	…	…
13. Lonyet	63·3	19·1	…	17·4	…	…

ANALYSES OF GERMAN SILVER—*continued.*

Authority.	Composition per cent.					
	Copper.	Nickel.	Cobalt.	Zinc.	Iron.	Lead.
14. D'Arcet . . .	50·0	18·7	...	31 2	...	...
15. Hiorns . . .	58·0	18·5		23·5	...	.
16. Smith . . .	60·0	18·8	3·4	17·8	...	...
17. Krupp . . .	58·3	19·4	...	19·4	...	2·9
18. Hiorns . . .	53·1	16·2	..	30 0	0·67	..
19. ,, . . .	55·6	15·7	...	28·7	...	...
20. ,, . . .	56·8	15·6	...	27·2	0·3	...
21. Lonyet . . .	62·4	15·0	...	22·1	...	.
22. Krupp . . .	57·8	14 3	...	27·1	..	0 8
23. Hiorns . . .	58·7	13·8	...	26·4	1 0	...
24. ,, . . .	57·0	13·4	...	27·6	2·0	..
25. Elsner . . .	57·4	13 0	...	26·6	3·0	...
26. Hiorns . . .	55 4	11·6	...	31·4	1·6	...
27. Lonyet . . .	62 6	10·8	...	26·5	..	.
28. Rochet . . .	59·1	9·7	...	31·2	...	..
29. Hiorns . . .	66·0	8·2	...	25·3	0·5	...
30. Krupp . . .	63·0	6·0	...	31·0		...

The same authority gives the composition of the various qualities of German silver made by the best makers in Birmingham, together with the trade names under which they are known:—

Name.	Composition per cent.		
	Copper.	Nickel.	Zinc.
Extra white metal	50	30	20
White metal	54	24	22
Arguzoid	48½	20½	31
Best Best	50	21	29
Firsts or best	56	16	28
Special firsts	56	17	27
Seconds	62	14	24
Thirds	56	12	32
Special thirds	56½	11	32½
Fourths	55	10	35
Fifths, for plated goods	57	7	36

The best of these alloys are somewhat costly; and for most purposes the quantity of nickel does not exceed 20 per cent.

As the result of a number of experiments on the relative composition of German silver, Hiorns concludes that, for alloys containing less than 16 per cent. of nickel the quantity of zinc should be 30 per cent. in order to give the best results; while with alloys containing more than 16 per cent. of nickel the quantity of zinc should be less than 30 per cent.

As regards the impurities found in German silver, those most often met with are iron, lead, and tin. Iron forms a solid solution with the alloy, with the result that it increases the strength, hardness, and elasticity of the alloy, and at the same time makes it slightly whiter. It follows that for some purposes the addition of 1 or 2 per cent. of iron may be an advantage. Tin, on the other hand, does not enter into solid solution in the alloy, but forms a eutectic which renders the metal brittle and unfit for rolling. It also makes the alloy decidedly yellow in colour when present even in small quantities. For ornamental castings, however, an alloy containing 1 or 2 per cent. of tin is frequently used. Lead does not alloy with German silver, but separates out as metallic lead, in the same way as already described in the case of brass. This metal is therefore purposely added to the extent of 2 or 3 per cent. when the metal is to be cast and subsequently worked, but is not permissible in metal that is intended for rolling. The remarks which have been made with regard to lead in brass apply equally to the case of German silver. Cobalt is occasionally found in small quantities, owing to its presence in the nickel, and has sometimes been purposely added; but it is an expensive metal, and does not appear to confer any properties upon the alloy to justify its presence.

German silver is made by melting the metals in the usual way in graphite crucibles. The separate metals, however, are not melted together; but are used in the form of alloys of copper and nickel and copper and zinc. This method answers the double purpose of more readily producing a homogeneous alloy and lessening the oxidation of the zinc. Shortly before pouring the metal a further small quantity of zinc may be added, to compensate for volatilisation and ensure thorough deoxidation of the alloy.

The metal is cast in iron moulds similar to those used in brass casting, but of different sizes. For ingots which are intended to be rolled into sheets the moulds are from 16 to 18 ins. in length, 1 to 1¼ ins. thick, and from 4 to 5 ins. wide; while for ingots for wire drawing the sizes are from 4½ to 5 ft. long, 1¼ ins. thick, and 3½ ins. wide. The method of casting is exactly the same as in the case of brass; but the melting-point of German silver being higher than that of brass, the casting has to be performed rapidly, or the crucible has to be returned to the furnace to be reheated.

From time to time various metals have been added to German silver for special purposes, and a great number of complex alloys have been patented; but very few of them appear to have met with any success. There are, however, a few exceptions which may be mentioned.

Platinoid is a German silver containing tungsten. It consists of 60 per cent. copper, 14 per cent. nickel, 24 per cent. zinc, and 1 to 2 per cent. tungsten. This alloy possesses a low electrical conductivity, and has therefore been largely used in the manufacture of electrical resistances. It should be pointed out, however, that many samples of platinoid fail to show even traces of tungsten on analysis.

German silvers containing silver were introduced long ago by Ruolz, and were used for making jewellery. The composition of the alloys varied, but they contained from 20 to 30 per cent. of silver, 25 to 30 per cent. of nickel, and 35 to 50 per cent. of copper. Similar alloys, but containing less silver, have been used for the subsidiary coinage of Switzerland. The percentage composition of these alloys was as follows:—

	20 Centimes.	10 Centimes.	5 Centimes.
Silver	15	10	5
Copper	50	55	60
Nickel	25	25	25
Zinc . . .	10	10	10

Several German silvers containing aluminium have been suggested, the aluminium acting as a deoxidiser. An alloy of this description containing 57 per cent. copper, 20 per cent. nickel, 20 per cent. zinc, and 3 per cent. aluminium, is largely used for typewriter parts. Magnesium is sometimes used for the same purpose, and an alloy containing 75 to 90 per cent of copper, 10 to 25 per cent. of nickel, and 1 to 2 per cent. of magnesium, is said to be largely used in Germany. The high cost of these alloys, however, is a serious drawback.

German silver can be readily soldered, the alloy used for this purpose being made more fusible than the German silver by having a larger proportion of zinc. The usual composition of German silver solder is: Copper 47 per cent., nickel 11 per cent., and zinc 42 per cent.

Phosphor-copper.

Copper and phosphorus combine very readily with the formation of a definite chemical compound corresponding to the formula Cu_3P. It has a bluish-grey metallic lustre, is very hard, and brittle enough to be easily reduced to powder. It forms with copper a simple series of alloys with a eutectic containing 8·2 per cent. of copper and melting at 704° C. Commercial phosphor-copper occurs in two varieties—one containing 15 per cent. of phosphorus, which is practically the compound Cu_3P; and the other containing 10 per cent. of phosphorus, consisting mainly of the eutectic. Both these phosphor-coppers are exceedingly brittle; this is a great advantage, as their chief use is that of a deoxidiser to be added to copper and copper alloys. A brittle substance which can be broken into small lumps or powdered, possesses obvious advantages when exact quantities have to be weighed out.

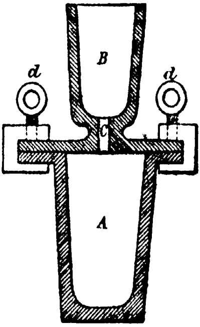

FIG. 64.—Phosphor-copper Crucible.

Phosphor-copper is made either by passing the vapour of phosphorus into molten copper, or over heated copper, or, more readily, by adding phosphorus to molten copper. An ingenious device for effecting the combination is described by Hiorns and illustrated in fig. 64. Phosphorus is placed in the lower vessel A, and the molten copper is poured in through the upper vessel B. Any phosphorus vapour which escapes combination in the lower vessel is caught as it passes through the molten metal in the upper vessel.

The usual method of preparing phosphor-copper is by adding phosphorus to molten copper. The cakes of yellow phosphorus are immersed in a solution of copper-sulphate until completely coated with copper. They are then dried carefully in sawdust, and plunged below the surface of the metal in the crucible by means of a pair of tongs.

Cupro-silicon.

The alloys of copper and silicon, like those of copper and phosphorus, are used mainly as deoxidisers in the manufacture of copper alloys. Commercial cupro-silicon is made in the electric furnace, and contains as much as 50 per cent. of silicon; but the alloys most generally used do not contain more than 35 per cent. These alloys are extremely brittle.

According to Guillet the alloys containing less than 7 per cent. of silicon consist of solid solutions; but beyond this point there is a eutectic which melts at about 800°.

Copper containing a small quantity of silicon, not exceeding 0·1 per cent., is much stronger than pure copper, and has been largely used for the manufacture of telegraph and telephone wires. For this purpose silicon is much better than phosphorus as a hardening agent for copper, the conductivity of the wire being considerably higher. The addition of phosphorus to copper is accompanied by a very marked increase in its electrical resistance.

Copper containing a small percentage of silicon has also been successfully used as a material for firebox plates.

Cupro-manganese.

Reference has already been made to the alloys of copper and manganese in connection with the manufacture of manganese-bronzes and brasses. The commercial alloys contain about 30 per cent. of manganese and sometimes from 2 to 4 per cent. of iron, and they appear to be homogeneous solid solutions of manganese in copper. They are principally used in the manufacture of the so-called manganese-bronzes, in which the manganese acts partly as a deoxidiser, while any excess of the metal is soluble in the bronze and imparts strength and hardness to it.

Simple alloys of copper and manganese containing from 4 to 6 per cent. of manganese are employed for firebox stays; but this appears to be the only useful application of the alloys.

Copper-magnesium.

Of late years the alloys of copper and magnesium have been extensively used as deoxidisers in the melting of copper alloys, and more particularly German silver. Magnesium unites with oxygen with even greater avidity than aluminium, and any excess of the metal above that required to reduce the oxides in the alloy appears to form a solid solution with the alloy, without injuring or materially affecting its properties.

The freezing-point curve of the series, which has been determined by M. Boudouard, is somewhat complex, and indicates the existence of three definite compounds, corresponding to the formulæ Cu_2Mg, $CuMg$, and $CuMg_2$. The curve, then, can be regarded as four curves representing respectively—

1. The alloys formed between copper and the compound Cu_2Mg.
2. The alloys formed between the two compounds Cu_2Mg and $CuMg$.
3. The alloys formed between the two compounds $CuMg$ and $CuMg_2$.
4. The alloys formed between the compound $CuMg_2$ and magnesium.

The microscopical examination of the alloys confirms the existence of the three compounds. As might be expected, almost the entire series of alloys are extremely brittle.

Copper-oxygen.

Copper possesses the somewhat unique property of forming a well-defined series of alloys with its own oxide. The alloys are a simple series, the eutectic, which is shown in photograph 50, containing 3·45 per cent. of cuprous oxide (Cu_2O), equivalent to 0·39 per cent. of oxygen. This behaviour of copper towards its oxide is of considerable importance, and must be taken into account when considering the properties of the copper alloys. Owing to the fact that the oxide separates in the spherical and not in the laminated form its influence on the mechanical properties of the metal is relatively small. Thus Hampe states that 0·45 per cent. of copper oxide (equivalent to 13 per cent. of eutectic) in pure copper does not affect its ductility, and only when 2·25 per cent. of oxide, or 65 per cent. of eutectic is exceeded, does the metal become short.

The influence of impurities on the condition in which oxide exists in copper is of considerable interest. Thus arsenic, which is present in nearly all commercial coppers and which forms a solid solution with copper, causes the copper oxide particles to aggregate or "ball up" until the eutectic structure disappears. This accounts for the fact that the eutectic structure is never detected in commercial coppers, even though they contain considerable quantities of oxygen. Photograph 63, for example, shows the oxide in a firebox copper containing no less than 1 per cent. of oxide or the equivalent of 29 per cent. of eutectic. It contains, however, 0·4 per cent. of arsenic, and this is quite sufficient to completely destroy the characteristic eutectic structure and cause the oxide to separate in massive form. The way in which the oxide particles of the eutectic coalesce is shown in photographs 51 and 52, which represent the eutectic mixture to which 0·08 per cent. of arsenic has been added.

Copper-arsenic.

The alloys of copper and arsenic are of some importance on account of the fact that in this country firebox plates and stays are made almost exclusively of copper containing arsenic. The complete series of alloys have been investigated by Bengough and Hill, who have shown that under normal conditions of cooling copper forms a solid solution with arsenic up to about 3 per cent., while in the case of slow cooling or annealing the solubility is considerably less. It is evident, therefore, that only those alloys containing very small percentages of arsenic are of any practical value, and as a matter of fact the actual percentage in practice rarely exceeds 0·5 per cent. It must be remembered, however, that the arsenic enters into solution not as metallic arsenic but as arsenide of copper (Cu_3As), and 1·8 per cent. of arsenide (corresponding to 0·5 per cent. of arsenic) has an appreciable effect in strengthening and stiffening the copper.

In addition to those already mentioned, a number of copper alloys are now manufactured for use in the preparation of special bronzes and brasses. These include copper-vanadium, containing 8 or 9 per cent. of vanadium; copper-titanium, containing 10 per cent. of titanium; copper-chromium, containing 10 per cent. of chromium; and copper-iron, containing 50 per cent. of iron.

TYPICAL COPPER ALLOYS.

Description of Alloy	Copper	Tin.	Lead	Zinc	Iron.	Alu-minium	Man-ganese	Nickel.	Phos-phorus.	Other Con-stituents.
Gun-metal, original Ordnance alloy	90·00	10·00								
,, Admiralty No 1 alloy	88·00	10·00		2·00						
,, Admiralty No 2*a*, to resist high pressure	86·00	13·00		1·00						
,, "Hydraulic" metal	83·05	10·81	0·10	6·00						
Bronze, British coinage	95·00	4·00		1·00						
,, for slide valves, Midland Rly	85·00	15·00								
,, ,, ,, ,, L. & Y Rly	84·50	10·00	5·00						0·50	
,, injector metal, L. & Y Rly	84·00	8·50	2·50	5·00						
,, Japanese art metal	82·70	4·70	9·90	1·80						
,, Chinese art metal	74·00	1·00	15·00	10·00						
,, "Electric" or telegraph metal	80·00	5·00	7·50	7·50						
Phosphor bronze, wire	92·85	6·50							0·31	
,, ,, rolled sheet	96·90	3·00							0·13	
,, ,, bearing	89·10	10·10							0·72	
,, ,, gear wheel	86·80	12·20							1·43	
Lead-bronze, antifriction alloy	78·07	8·15	13·78							
,, ,, "Plastic" bronze bearing metal	64·13	5·05	30·11					0·73		
,, ,, "Plastic" bronze bearing metal	63·58	5·30	28·88	0·85				1·04		
Bell metal ("Big Ben")	75·80	24·20								
Brass, for high-pressure turbine blades	94·85			4·83	0·32					
,, for sheet, wire, tubes, etc	70·00			30·00						
,, for condenser tubes, Admiralty specification	70·00	1·00		29·00						
,, ordinary, for tubes, sheets, etc.	67·00			33·00						
,, for castings	57·00			43·00						
,, for castings to be machined	60·00		2·00	38·00						
,, ,, ,, ,, ,,	54·00		2·00	44·00						
Muntz metal	60·00			40·00						
Aich's metal	60·00			38·20	1·80					
Sterro metal	55·50			42·00	2·50					
Delta metal	60·00	1·74	1·41	35·66	0·76				0·16	

TYPICAL COPPER ALLOYS—*continued*

Description of Alloy	Copper	Tin	Lead	Zinc	Iron	Aluminium.	Manganese	Nickel	Phosphorus	Other Constituents
Delta metal	55·10	..	0·37	43·47	1·08	..			0·10	
Special brass, for **extrusion**	55·10	0·77	0·52	41·89	0·84	0·07	0·36	0·28		
Manganese-bronze	93·31	0·27			1·56	..	3·80	0·52		
,, ,,	69·00			24·21	1·57	4·88	0·24			
,, ,,	58·55	1·95		35·41	1·62		0·62			
,, ,,	59·15	1·07		37·76	0·80	0·38	0·52			
,, ,,	56·16	1·17	0·38	40·62	0·37	0·19	1·11			
,, ,,	54·94	1·36		[illegible]	1·16	0·35	0·47			
,, ,, containing **nickel**	56·01	1·03		39·57	1·06	0·10	trace	2·23		
Aluminium-bronze	90·00					10·00				
,, ,,	92·66					7·34				
,, ,,	88·40				0·21	9·14				Silicon 1·73
,, ,, containing nickel	87·00					10·50		4·50		
Aluminium-brass	61·28		0·07	35·33	1·10	2·20				
Silicon-bronze	98·55	1·40								Silicon 0·05
Copper-manganese, for firebox stays, etc	90·40				1·82		7·78			
Copper-arsenic, for firebox stays, etc	99·30		0·07					0·05		Arsenic 0·48
Copper-nickel, ,, ,, ,,	98·05							1·92	0·0[illegible]	
,, ,, coinage alloy	75·00							25·00		
,, ,, for sheet, bullet casing etc	80·00							20·00		
Constantan, electric resistances and thermocouples	60·00							40·00		
German silver	59·10			20·40	0·30			20·20		
Sterline	68·52		0·15	12·84	0·76			17·88		
Argozoil, for ornamental castings	54·06	2·00	2·00	25·06				14·00		
Platinoid, electric resistance wire	54·04			20·42	0·47		0·15	27·77		
Manganin, ,, ,, ,,	82·12				0·57		15·02	2·29		
Nickelin, ,, ,, ,,	68·00							32·00		
,, ,, ,, ,,	55·31			13·10	0·43			31·07		
Resistin, ,, ,, ,,	84·32	0·10			1·92		13·45			Silicon 0·15
Aluminium silver	57·00			20·00		3·00		20·00		
Platinum, for **valve seatings**	32·55	12·72			0·48	0·32		53·80		
Monel metal	33·00				6·50	0·50		60·00		

Alloy.		Chemical	Mechanical.			
			Tensile. Tons per sq. in.	Elastic Limit Tons per sq. in.	Elongation per cent.	Other Tests.
Gun-metal	Admiralty No 1. Used for steam valves, etc., where a high quality alloy is required.	Copper, 88 Tin 10 Zinc, 2% (max.) Max. allowable variation 1%	14		7.5 in 2 ins	
Gun-metal	Admiralty No. 2*a*. To resist high water pressure. Used for gun mountings, gun-elevating cylinders, etc.	Copper, 86% Tin, 13 Zinc, 1%	14		3.5 in 2 ins	Hydraulic test of 6000 lbs. per sq. in.
Brass	British Standard specification for tubes for locomotive boilers	Copper 70% Zinc 30% or Copper, 66.7% Zinc, 33 [illegible] In either case not more than 0.75% of materials other than copper and zinc allowed.			...	*Bulging or Drifting Test.*—The tubes must stand bulging or drifting without showing either crack or flaw until the diameter of the bulge or drifted end measures not less than 25 per cent greater than the original diameter of the tube. *Flanging Test.*—The tubes must stand flanging without showing either crack or flaw, until the diameter of the flange measures not less than 25 per cent greater than the original diameter of the tube. *Flattening and Doubling-over Test.*—The tubes must be capable of being flattened down until the interior surfaces meet, and then doubled over on itself, without showing crack or flaw. *Hydraulic Test.*—750 lbs. per sq. in.

TYPICAL SPECIFICATIONS—*continued.*

Alloy.		Chemical.	Mechanical.			
			Tensile. Tons per sq in	Elastic Limit. Tons per sq in.	Elongation per cent.	Other Tests.
Brass	Admiralty specification. For condenser tubes.	Copper, 70% Zinc, 29% Tin, 1%		...	...	
Naval brass	Admiralty specification	Copper, 62% Zinc, 37% Tin, 1%	Round bars $\frac{3}{4}$ in. and under. 26	...	10 on 2 ins	All bars must be capable of—(*a*) being hammered hot to a fine point; (*b*) being bent cold through an angle of 75° over a radius equal to the diameter or thickness of the bars. All naval brass sheets are, when cold, to be capable of being bent double without fracture over a radius equal to the thickness of the sheet.
			Above $\frac{3}{4}$ in, square and hexagonal. 22		10 on 2 ins.	
High tension brass.	Admiralty specification For propeller blades and to resist high water pressure	Copper, 56·6% Zinc, 39·9% Tin, 1·0% Iron, 1·45% Manganese, 0·8% Aluminium 0·25%	Cast 28	15	15 on 2 ins	Hydraulic test of 6000 lbs. per sq. in.
			Forged 28		28 on 2 ins.	
Phosphor-bronze.	Admiralty specification. For castings.	Copper, 90·0% Tin, 9·7% Phosphorus, 0·3%	17	...	15 on 6 ins.	To stand bending over a 2-in. bar until the two sides are parallel without any signs of cracking.
Phosphor-bronze.	Admiralty specification. Wire for braiding electric cables.	Not less than 5% tin.	20 (min.)	...	42 (min.) on 5 ins.	
Phosphor-bronze	Admiralty specification. For bearings.	Copper, 85·0% Phosphorus, 0·45% (min.). Tin, remainder.	...	...	...	

Copper	British Standard specification. For firebox plates.	A. Copper, not less than 99%. Arsenic, 0·35 to 0·55%. B. Copper, not less than 99·25%. Arsenic 0·25 to 0·45%.	14 (min.)	...	35 on 8 ins (min.)	*Bend Test.*—Pieces of the plate shall be tested both cold and at a red heat by being doubled over on themselves without showing either crack or flaw on the outside of the bend
Copper	British Standard specification. For locomotive stay bolts, rivets, etc.	Copper, not less than 99·25% Arsenic 0·15 to 0·35%.	14 min.		40 (min.) on a gauge length not less than 8 times the diameter.	*Hammering or Crushing Down Test.*—A piece of rod 1 in. long shall be placed on end and hammered or crushed down to a thickness of ⅜ in. without showing either crack or flaw on the circumference of the resulting disc.
Copper	British Standard specification For tubes for locomotive boilers	Copper not less than 99%. Arsenic, 0·35 to 0·55%.	..	..	..	*Bulging or Drifting Test.*—The tube must stand bulging or drifting, without showing either crack or flaw, until the diameter of the bulged or drifted end measures not less than 25 per cent greater than the original diameter of the tube. *Flanging Test.*—The tubes must stand flanging, without showing crack or flaw, until the diameter of the flange measures not less than 40 per cent. greater than the original diameter of the tube. *Flattening and Doubling Over Test.*—The tube must be capable of being flattened down until the interior surfaces of the tube meet, and then doubled over on itself, the bend being at right angles to the length of the tubes. *Hydraulic Test.*—750 lbs. per sq. in.

CHAPTER XI.

WHITE METAL ALLOYS LEAD, TIN, AND ANTIMONY.

THE alloys of these metals are very largely employed in the industrial world, and are usually met with under the name of "white-metal." The term is applied indiscriminately to any of the alloys, whether composed of only two of the metals or all three together, but, as each series of alloys has its distinct uses, it will simplify matters to deal first with the three possible series of binary alloys—viz. lead-tin, lead-antimony, and tin-antimony—and then with the triple alloys.

Alloys of Lead and Tin.—These metals do not form compounds or solid solutions, but mix in all proportions, thus forming the simplest series of binary alloys. The freezing point curve of the series has already been referred to, and it is only necessary to repeat that the eutectic contains 37 per cent. of lead, and melts at 182.5°. On either side of this point the alloys consist of one or other of the metals surrounded by the eutectic. The percentage of tin in the cast alloys can be roughly estimated by the appearance of the surface. Those rich in lead possess the dull bluish colour characteristic of that metal; while the alloys rich in tin have a white surface, which has a slight yellow superficial deposit of oxide of tin. The alloys containing more than 25 per cent. of lead will leave a mark when drawn across paper.

The alloys of lead and tin are used principally in the manufacture of solders, toys and cheap jewellery, and pewter.

Solders are very variable in composition according to the quality of the metal to be soldered. Those rich in tin are, of course, the most valuable, and the alloys are known, according to the amount of tin they contain, as "common," "medium," and "best."

For soldering tin and alloys rich in tin a solder rich in tin must be employed, while for lead and alloys rich in lead a solder rich in lead is used. Probably the alloy most commonly employed is that containing 66 per cent. of lead and 34 per cent. of tin, or two parts lead to one of tin. Equal parts of lead and tin give the alloy known as "Plumbers' Solder," while 60 per cent. tin and 40 per cent lead is known as "Tinsmiths'" or "Tinmen's Solder." For electrical work an alloy containing 95 per cent. of tin is largely used

The best solders should be made from pure metals and not from scrap, as impurities even in small quantities have a pronounced influence on the quality of the alloys Both zinc and antimony have an injurious effect, although the latter is sometimes added as it improves the surface appearance of the metal. Phosphorus, on the other hand, may be added in small quantities to effect complete deoxidation and render the solder more fluid

The suitability of the alloys of lead and tin for soldering is dependent on the fact that these metals do not form compounds or solid solutions, and, in consequence, almost the entire series of alloys is composed of a metal and a eutectic mixture at temperatures lying between the melting-points of these two the alloy is only partly solid, or in the pasty condition which enables it to be easily applied in soldering. Thus, in the case of the alloy referred to above containing 66 per cent. of lead, there is a range of temperature of 60° during which the alloy is in a pasty condition. The eutectic itself and the alloys in its immediate neighbourhood are not suitable for solders, but they solidify with an exceedingly bright surface, and have been used for making imitation jewels, sometimes known as Fahlum brilliants, for stage purposes The eutectic alloy is cast in moulds with facets resembling the cutting of diamonds. Alloys rich in lead are used for making toys, such as lead soldiers, etc. These, however, contain very little tin seldom more than 4 or 5 per cent.

The best known of the lead-tin alloys is that commonly known as pewter. This alloy is largely used, and its composition varies considerably. When intended for the manufacture of drinking-vessels it is essential that the alloy should be rich in tin. This is evident from the consideration of the constitution of these alloys, for those containing more than 37 per cent. of lead (that is to say, more lead than is sufficient to form the eutectic of the series) will contain free lead in a form readily corroded and dissolved by acid liquids. In order to avoid risk of lead-poisoning, therefore, pewter should contain at least 63 per cent. of tin, and in France the law prohibits the use of pewter containing more than 18 per cent. of lead for drinking-vessels.

A large quantity of pewter is used in the arts. For this purpose the composition may be altered to suit the requirements of the work. Copper in small quantities is a frequent constituent of pewter. It produces a harder alloy, but, if present in more than small quantities, has an injurious effect upon the colour of the pewter.

Lead and Antimony.—As in the case of the lead-tin alloys, these metals do not form compounds or solid solutions, but produce a simple series of alloys with a eutectic containing 13 per cent. of antimony and melting at 245°. On one side of this point the alloys consist of lead embedded in eutectic, and, on the other side, antimony embedded in eutectic. The useful alloys of lead and antimony are somewhat limited; those consisting principally of lead with small amounts of antimony, introduced as a hardening agent, being the most useful. An alloy, however, containing 67 per cent. of lead and 33 per cent. of antimony is occasionally met with, and is used in making the keys of wooden wind instruments. Antifriction metals consisting of lead and antimony are still sometimes found, but these have been superseded by the more efficient triple alloys.

Lead containing antimony up to about 4 per cent. is largely used in the manufacture of the framework of accumulator plates, as the alloy is stronger than pure lead, less liable to buckle, and cheaper. Antimonial lead is also used in the manufacture of shot and bullets.

With the addition of small quantities of other metals the alloys of lead and antimony are extensively used as type-metal. The essential requirements of a good type-metal are: (1) that it shall give good, sharp castings; and (2) that it shall be sufficiently strong to withstand the necessary wear and pressure without losing its form. The first of these requirements is fulfilled by the alloys containing not more than 15 per cent. of antimony, which possess the property of expanding on cooling; but they are not strong enough to stand hard wear. In order to increase the strength of these alloys a certain quantity of tin is added, which forms a hard compound corresponding to the formula $SnSb$, and this compound crystallising out in the soft alloy has the effect of considerably increasing the compressive strength of the mass, without otherwise altering the character of the alloy. The composition of type-metal varies considerably. An alloy containing lead 50, tin 25, and antimony 25 is said to give the best results for high-class work; but the price of such an alloy is too high on account of the tin it contains, and a more usual composition is approximately lead 60, antimony 30, and tin 10 or even less. Plates for music engraving of somewhat similar composition are used abroad, but in this country the best music printing is done on pewter plates.

Modern printing machines such as the monotype and linotype use an even cheaper alloy, in which the tin is often as low as 3 per cent. and the lead as high as 85 per cent.

Alloys of lead and antimony are frequently used in the construction of pumps required for dealing with corrosive liquids, and, as it is important to know the strength of these alloys, Prof. Goodman has made a number of very complete determinations. The alloys selected had the following compositions —

Number.	Antimony.	Lead.	Tin.
1	10	90	...
2	13	87	...
3	15	85	..
4	15	80	5

and the tests were carried out with the object of determining—

(1) The tensile strength and elasticity.
(2) The compressive strength and elasticity.
(3) The crushing strength.
(4) The bending strength.
(5) The shearing strength.

The results of these tests are given in the tables on p. 238.

Tin and Antimony.—These metals give rise to an extremely interesting but considerably more complex series of alloys than

Number.	Diameter in Inches.	Sectional Area in Sq. In.	Elastic Limit in Tons per Sq. In.		Maximum Stress in Tons per Sq. In.		Young's Modulus of Elasticity Tons per Sq. In.		Reduction in Area per cent.	Extension per cent. on 10 in.
			Tension	Compression.	Tension.	Compression.	Tension	Compression		
1	2·248	3·969		1·39	...	...	...	1740		
	1·489	1·741	0·93	...	3·14		1700	...	1·3	0·4
	1·510	1·791	1	.	3·32		1690		1·7	1·1
	2	3·141	...		...	7·98		.		..
	2	3·141			..	7·20	..	..	...	.
2	2·246	3·962		1·0	.		.	1800		
	1·490	1·744	0·95	..	3·28	...	1780		3·7	2·5
	1·503	1·774	0·90		3·10	.	1690	Broke in shoulder	...	1·3
	1·998	3·135	...		...	7·12	...	...	...	...
	1·999	3·138	.			7·31				...
3	2·245	3·958		1·07		..		1820	...	...
	1·510	1·790	0·92	..	2·71	..	1750		2·4	0·9
	1·508	1·786	0·92	...	3·07		1680	Broke in shoulder	..	1·4
	2	3·141	.	...	...	7·49		.	...	...
	2	3·141				7·49	...	...	...	...
4	2·245	3·958	..	1·01	.	.		1890	...	
	1·497	1·760	0·80		2·27		1830	Broke in shoulder	..	...
	1·496	1·758	0·83	...	2·80	.	1660	Ditto	...	0·5
	2	3·141	...	...	.	7·00		.	.	...
	2	3·141	..			6·95		...	...	...

Number.	Breadth of Section in Inches.	Height of Section in Inches.	Breaking Load in Tons.	Modulus of Rupture in Tons per sq. in.	Final Deflection in Middle of Beam.	Shearing Strength in Tons per sq. in.	Ratio of Shearing Strength to Tensile Strength.
	b.	*h.*	*W.*	*fm.*	In.	*fs.*	
1	1·018	2·039	1·25	5·31	0·125	2·29	0·71
	1·025	2·030	1·25	5·33	0·143	2·28	
2	1·016	2·047	1·19	5·02	0·095	2·14	0·68
	1·005	2·042	1·18	5·07	0·134	2·18	
3	1·012	2·047	1·11	4·72	0·116	2·18	0·75
	1·025	2·047	1·09	4·58	0·117	2·16	
4	1·020	2·045	1·12	5·11	0·085	1·95	0·76
	1·025	2·045	1·09	4·59	0·075	1·92	

those just considered. The freezing-point curve, as determined by Reinders, indicates that the alloys containing antimony up to 10 per cent. consist of tin and a eutectic; but beyond 10 per cent. the characteristic cubical crystals of the compound SnSb make their appearance, and when 50 per cent. is reached the alloy becomes homogeneous and consists entirely of this compound. With more than 50 per cent. of antimony neither a eutectic nor a new constituent makes its appearance; but the crystals gradually change their form and become more and more like those of antimony. Evidently, then, this is a case of a compound being isomorphous with a pure metal; and this fact accounts for the abnormal freezing-point curve, which apparently fails to indicate the existence of a compound. The conductivity of the alloys (as determined by Matthiessen) and the electromotive force of solution (as determined by Laurie) also fail to indicate the existence of a compound for the same reason.

The alloys of tin and antimony together with small quantities of other metals constitute the class of alloys known under the name of **Britannia metal.** The following table shows the composition of a number of these alloys:—

Alloy.	Tin	Antimony.	Copper	Zinc	Bismuth	Lead	Other Metals.
Britannia metal (Eng.)	94	5	1	.	..	...	...
,, ,,	90	6	2	...	2		.
,, ,,	90	7	3		...		...
,, ,,	89·3	7	1·8			1·8	
,, ,,	85·5	9·7	1·8	3·0			...
,,	75·0	8·5		...	8·0	8·5	.
,, (sheet)	90·6	7·8	1·5		.	...	
,, (cast)	90·6	9·2	0·2				
Queen's metal . .	88·5	7·1	3·5	0·9			
,, . .	88·5	7·0	3·5	...	1		
Ashberry metal . .	80	14	2	1	...	...	3
,, . .	79	15	3	2			1
Minofor . . .	68·5	18·2	3·3	10			...
German metal . .	72	24	4	.	...	...	..
,, . .	84	9	2	5	...	...	.
,, . .	20	64	10	6	...	...	..

The presence of copper in Britannia metal produces a harder and less ductile alloy, and has an injurious effect upon the colour if present in more than small quantities. Zinc and iron also increase the hardness and brittleness of the alloy, and are not desirable constituents. Lead, on the other hand, may be added with advantage where a very fluid metal is required for casting; but the amount added should be small, if the colour of Britannia metal is to be retained.

In all these alloys the antimony has the effect of hardening the tin, so that it is more easily worked and takes a finer polish. The best castings are obtained from brass moulds previously heated and coated with lamp black. Britannia metal is extensively used in the manufacture of such articles as tea- and coffee-pots, mugs, etc., and also for taps.

The triple alloys of lead, tin, and antimony are largely used as antifriction alloys, and will be considered under that heading.

LEAD, TIN, AND ANTIMONY ALLOYS.

	Lead.	Tin	Antimony.	Copper.
Electrotype metal	93·0	3·0	.	...
Linotype metal	85·0	3·0	12·0	..
,, ,,	83·0	5·0	12·0	
Stereotype metal	82·5	4·5	13·0	
,, ,,	82·0	6·0	12·0	
,, ,, (old)	68·0	14·0	18·0	
,, ,, ,,	35·0	60·0	5·0	..
Monotype metal	74·0	8·0	18·0	...
Type metal	77·5	6·5	16·0	
,, ,,	70·0	10·0	18·0	2·0
,, ,,	63·2	12·0	24·0	0·8
,, ,,	60·5	14·5	24·2	0·7
,, ,,	60·0	10·0	30·0	...
,, ,,	50·0	25·0	25·0	.
Solder (for electrical work)	5·0	95·0	...	..
,, (tinsmiths')	10·0	60·0	.	
,, (ordinary)	50·0	50·0		
,, ("plumbers' sealed")	66·6	33·3	.	...

CHAPTER XII.

ANTIFRICTION ALLOYS.

In a perfectly adjusted and lubricated bearing there is a thin layer of oil between the journal and the bearing, so that the metals never come in contact, and the friction, as has been shown by Osborne Reynolds, and others, is merely that between a solid and a liquid, and depends solely upon the nature of the lubricant. It follows that the nature of the metal of which the bearing is composed is immaterial; but such perfect adjustment is not attained in actual practice, and the problem presents itself of finding a metal or alloy sufficiently plastic to mould itself to the shape of the shaft, thus automatically rectifying imperfections of adjustment, and at the same time offering a minimum of friction. The use of lead was first suggested, according to Thurston, by Hopkins; but this metal is too soft and easily deformed, and soon gave place to white-metal alloys. Apparently the manufacture of these alloys was not entirely satisfactory, for in 1852 Mr Nozo of the Compagnie des Chemins de fer du Nord stated that they could be used advantageously with small load and medium speed but that for railroad vehicles they were not satisfactory. Since the publication of this statement antifriction metals have been greatly improved, and they are now very largely used. Mr Salomon, the chief engineer of the Chemins de fer de l'Est, has stated that the statistics on that railway have shown a decided advantage in favour of white metal over bronze; and Mr Chabal, the assistant engineer of the Paris, Lyon, Méditerranée Railway records that white-metal bearings become heated much less often than bronze, the wear also being less.

Since the introduction of white-metal bearings an immense number of so-called antifriction metals have been placed upon the market (some of which are given in the tables on pp. 251–256), and it becomes a matter of importance to determine what are the essential characteristics of a good bearing metal and to what extent these antifriction metals possess those characteristics.

In 1820 Rennie showed that the friction between two bodies under pressure increases proportionately to the pressure until a certain point is reached, when the two surfaces begin to rub against one another, causing a sudden increase in the coefficient of friction and consequent heating of the bodies. The pressure required to produce this sudden increase in the friction is greater with hard metals than with soft, and, at the same time, the coefficient of friction is smaller with hard metals than with soft ones.

The first conclusion we arrive at, then, is that a bearing metal should be as hard as possible. But this conclusion assumes a perfectly adjusted bearing in which contact between the shaft and the bearing is perfectly uniform—a condition which is rarely met with, especially in the case of a shaft supported by a number of bearings. If contact only takes place at a few points, the result will be heating and cutting. The second requirement of a good bearing metal, therefore, is that it must be sufficiently plastic to adapt itself to any imperfections of adjustment. A combination of these two requirements, hardness and plasticity, can only be obtained by having a body consisting of small, hard particles embedded in a plastic matrix; and this result is most easily produced by alloying a soft metal, such as lead or tin, with one or more metals which form definite compounds capable of crystallising out in the cooling mass. This, in fact, is the structure of antifriction alloys; but much depends, as will be seen presently, on the size and number of the hard crystals

For the sake of convenience, the bearing metals may be divided into five groups:—

I. Alloys consisting essentially of tin, containing compounds of tin and antimony, and tin and copper. These form a very large class.

II. Alloys consisting essentially of lead, or lead and tin, containing a compound of tin and antimony. These alloys are largely used on account of their low price.

III. Alloys consisting essentially of a solid solution of copper and tin (or copper and zinc), and containing compounds of copper and tin, copper and phosphorus, etc

IV. Alloys consisting essentially of a solid solution of copper and tin (sometimes containing zinc, nickel, etc), and containing free lead. These constitute an important class of bearing metals.

V. Alloys other than those described above.

Alloys of Group I.—In all the alloys of tin, copper, and antimony in which the percentage of tin preponderates, only two definite compounds are formed, viz. a compound of tin and antimony, which crystallises in well-defined cubes and which is the same compound as that found in the binary alloys of tin and antimony. Its composition corresponds to the formula SnSb, and, according to Charpy, it is less hard and less brittle than pure antimony. The other compound is that found in the binary alloys of copper and tin, crystallising in hard needles, often forming stars, and having a composition corresponding to the formula

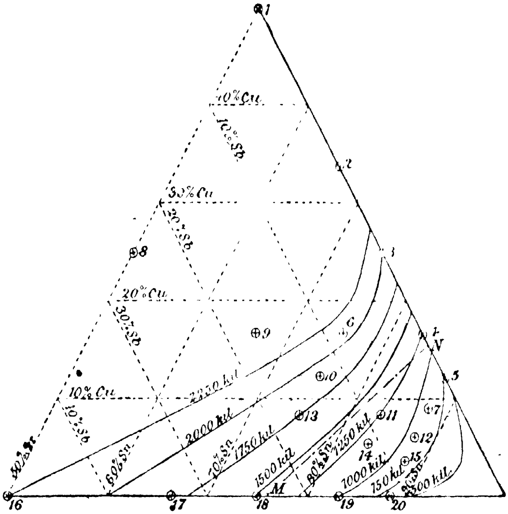

FIG. 65.—Compressive Strength of the Alloys of Tin, Copper, and Antimony.

$SnCu_3$ Both these compounds can be seen on a polished surface of the alloy, but etching with hydrochloric acid renders them more apparent. Photograph 35 illustrates the structure of a typical bearing metal of this type.

Charpy has examined twenty alloys of copper, tin, and antimony, and his results on the compressive strength of these alloys, which were carried out on test pieces 15 mm. in height and 10 sq. mm. sectional area, are given in the following table, and are also plotted in the form of a triangular diagram (fig. 65). The curved lines represent the loads producing a compression of 0·2 millimetre.

Number of Alloy.	Composition.			Load corresponding to a Compression of 0·2 mm.	Load corresponding to a Compression of 7·5 mm.
	Tin.	Copper.	Antimony.		
1	50	50	.	Broke without deformation.	
2	66	34		2810 kgs.	Broke
3	75	25	..	2000 ,,	,,
4	83	17		1325 ,,	2000
5	88	12	..	550 ,,	1550
6	75	8	17	2075 ,,	Broke.
7	88	4	8	875 ,,	2258
8	50	25	25	3760 ,,	Broke.
9	66	17	17	2780 ,,	,,
10	75	12·5	12·5	1730 ,,	,,
11	83	8·5	8·5	1200 ,,	2550
12	88	6	6	980 ,,	2550
13	75	17	8	1780 ,,	2550
14	83	11·5	5·5	1330 ,,	2750
15	88	8	4	1000 ,,	2475
16	50	.	50	2220 ,,	Broke.
17	66		34	1790 ,,	,,
18	75		25	1500 ,,	2600
19	83	...	17	1000 ,,	2650
20	88	..	12	600 ,,	2150

Alloys 1, 2, 3, 6, 8, 9, and 16 broke at the beginning of the compression, and Nos. 4, 10, 13, and 18 developed internal cracks before a compression of 7·5 mm. was reached. It follows that all these alloys are too hard, so that the line MN may be regarded as the limit of the useful alloys, and within this limit the alloy represented by No. 14 of the series has the greatest compressive strength. Alloys of approximately this composition are used by several railway companies for car bearings. Charpy states that the best alloys of this group should probably not differ from this composition by more than 3 or 4 per cent.

The method of casting and the rate of cooling of these alloys are of the utmost importance, and this subject has been carefully studied by Behrens and Baucke. They have shown that the hardness of the matrix of the alloy varies with the rate of cooling. In a rapidly cooled bearing this portion of the alloy solidifies with a greater percentage of copper and antimony, and its hardness may reach 2, tin being 1·7, while in a slowly cooled sample it may be as low as 1·6.

The size and number of the tin-antimony crystals also depends on the rate of cooling of the mass. In slowly cooled samples the crystals measure as much as 0·5 mm., while in chilled samples the crystals are small and imperfectly formed and can hardly be detected. Both these structures are met with in bearings which have become heated in service, whereas the structure of bearings which have proved satisfactory in service is intermediate between these two, the crystals being well formed and numerous, but not exceeding 0·25 mm.

As regards the proper temperature for casting, Behrens and Baucke cast three experimental bearings—one with a red-hot core, one with a core cooled by running water, and one with a core at 100° C. The first of these showed large tin-antimony crystals measuring 0·5 mm., and tin-copper crystals measuring 0·2 mm.; the second showed the confused structure of a chilled casting; and the third showed small tin-antimony crystals measuring 0·25 mm. The three bearings were then submitted to a practical test in the following manner. They were turned so as to fit a polished steel mandrel 15 mm. in diameter, which was capable of being rotated at a speed of 1600 revolutions per minute. The bearings were arranged so that the pressure on the blocks could be varied, and the rise in temperature was determined by means of thermometers fitted into holes in the blocks by soft amalgam. The increase in temperature, after running for one minute with pressures up to 3 kilograms per sq. cm., was as follows:—

	0·3 kg.	0·4 kg.	0·6 kg.	1·2 kg.	3 kg.
Red-hot core . .	0·65	1·60	1·72	2·62	4·64
Cold core . .	0·50	0·82	1·12	1·50	3·80
Core at 100° C. .	0·64	0·64	0·74	0·75	1·64

At the end of the experiment the chilled bearing showed irregular grooves and scratches, and the slowly cooled bearing was also badly scratched and grooved. The bearing cast at 100° C. showed the tin-antimony cubes partly rounded and the matrix surrounding them worn away, giving the impression that they might eventually be loosened and removed from their places. Evidently this actually occurs, for Behrens and Baucke submitted the oil from the bearings to a microscopical examination and found that it contained small spherical bodies like small drops of mercury, whereas the oil from bearings cooled too slowly or too quickly contained angular fragments. As the result of these observations Behrens and Baucke conclude that in a properly cast bearing the brittle rods of the tin-copper compound are crushed; and, acting as an abrasive, loosen and round the rectangular tin-antimony crystals, the result being that the bearing becomes practically a ball-bearing, with a rolling friction taking the place of a sliding friction. In a bearing which has been cooled too quickly the absence of the rectangular tin-antimony crystals prevents the formation of these spherical particles, and in a slowly cooled bearing the large crystals are broken instead of being rounded.

A study of the causes giving rise to heated bearings has shown that, in addition to the obvious cause of lack of proper lubrication, excessive heating is usually caused by: (1) defective crystallisation, due to the cooling taking place either too quickly or too slowly, usually the latter; (2) the presence of dross or scum in the metal; and (3) segregation of the metals, due to improper mixing or an attempt to alloy the metals in wrong proportions.

Alloys of Group II.—Before dealing with the triple alloys of this group it may be well to consider the simple alloys of lead and antimony, as they were formerly extensively used as antifriction alloys and their properties have been carefully studied by Charpy.

It will be remembered that lead and antimony give rise to simple alloys without the formation of any chemical compound. The eutectic contains 87 per cent. of lead and 13 per cent. of antimony, and on either side of the eutectic point the alloys consist of a single metal, lead in the one case and antimony in the other, surrounded by the eutectic.

Charpy has determined the compressive strength of these alloys, and his determinations of the loads corresponding to a permanent set of 0·2 mm. and 7·5 mm. in the case of pure lead, pure antimony, and seven alloys containing from 10 to 60 per cent. of antimony, are given in the following table:—

Composition of Alloy.	Load corresponding to a Permanent Set of 0·2 mm.	Load corresponding to a Permanent Set of 7·5 mm.	Remarks.
	Kilograms.	Kilograms.	
Pure lead . .	100	500	
10% antimony .	650	1300	
17·5% ,,	650	1450	
20 ,, .	760		Broke at 1250 kgs.
30 ,,	770		,, 1400 ,,
33 ,, .	800		,, 1400 ,,
50 ,, .	950	..	,, 1175 ,,
60 ,, .	1060	...	,, 1700 ,,
Pure antimony	..		Broke at 1150 kgs. without any appreciable compression

It will be noticed that the compressive strength increases with the increase of antimony until the eutectic is reached. On passing this point, however, there is only a slight increase in the compressive strength, due, as Charpy points out, to the fact that the antimony grains are isolated and merely transmit the load to the eutectic in which they are embedded. But when the antimony grains become sufficiently numerous to come in contact with one another they bear a portion of the load and the alloy becomes brittle, the brittleness increasing as the proportion of the plastic eutectic decreases.

In the alloys composed of lead, tin, and antimony the only compound formed is that of tin and antimony. This compound is the same as that which occurs in the tin-copper-antimony alloys, and it forms solid solutions with antimony.

The results of compressive tests on ten of these alloys are shown in the following table, and the curves corresponding to loads of 500, 750, 1000, and 1250 kilograms are plotted in the triangular diagram (fig. 66). Alloys possessing a greater compressive strength than 1250 kilograms were brittle, and Nos. 7, 8, and 9 of the series tested were badly cracked.

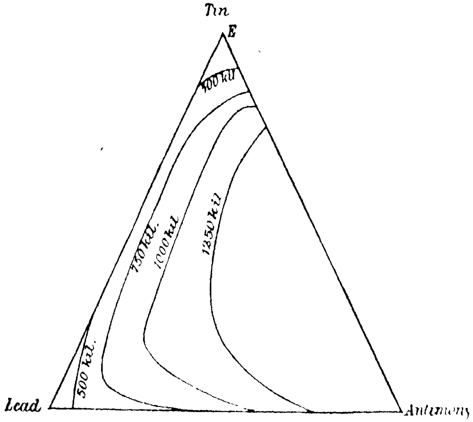

FIG. 66.—Compressive Strength of the Alloys of Lead, Tin, and Antimony

Antimony increases the hardness of the alloys, and should not exceed 18 per cent. if the alloys are not to be brittle.

No. of Alloy	Composition.			Load corresponding to a Compression of 0·2 mm.	Load corresponding to a Compression of 7·5 mm.
	Lead.	Tin.	Antimony		
				Kilograms.	Kilograms.
1	...	100	...	300	1060
2	20	80	..	600	1750
3	40	60		650	1475
4	60	40		600	1400
5	80	20		475	1150
6	10	80	10	1100	2700
7	20	60	20	1350	2200
8	40	40	20	1150	1825
9	60	20	20	1050	1700
10	80	10	10	800	1775

Charpy states that the alloys of lead, tin, and antimony are similar to those of lead and antimony; but, owing to the solubility of the compound SnSb in the antimony, the addition of tin diminishes the hardness and brittleness of the hard grains and also increases the compressive strength of the eutectic alloy For these reasons the alloys of lead, tin, and antimony are superior to those of lead and antimony alone. The tin must be present to the extent of more than 10 per cent., but not necessarily more than 20 per cent, and the antimony may vary between 10 and 18 per cent.

The alloys of this group frequently give results equal if not superior to those obtained with genuine Babbitt metal, but troubles are occasionally encountered, and in an interesting paper read before the American Society of Testing Materials, Lynch gives an account of a valuable research carried out in the works of the Westinghouse Electric and Manufacturing Company with the object of ascertaining the reason of the lack of uniformity in results occasionally shown by the lead alloys

Mechanical tests, Brinell tests, and a large number of friction tests, both in the laboratory and in service, were made without throwing any light on the subject Finally, however, it was found that a hammer test gave the most reliable indications of the behaviour of the alloys in service A drop-hammer was devised, and the test samples were prepared by casting the metal in a mould giving castings 1¼ ins. in diameter and $\frac{5}{16}$ in. thick, which were then turned to 1 in in diameter and ¼ in. thick. The test sample was subjected to repeated blows under the drop-hammer, measurements of the thickness being taken at frequent intervals. The results showed that alloys of the same composition might prove either hard and brittle, soft and brittle, soft and plastic, or hard and tough according to the temperatures to which they had been heated and at which they had been poured. The conclusion drawn from the results of a large number of tests was that the lead alloys were far more susceptible to the influence of pouring temperature than the tin alloys, and that the range of temperature necessary to give the best results was relatively small. For the particular alloy tested a temperature of 450° to 470° was found to give the best results

Alloys of Group III.—Although these alloys are, strictly speaking, not antifriction alloys, they are largely used for bearings and other parts of machinery subject to frictional wear. Their constitution has already been considered, and it is only necessary to repeat that in the case of the copper-tin alloys containing more than 9 per cent of tin the hard compound $SnCu_3$ separates out while in the case of the alloys containing phosphorus, a hard compound PCu_3 separates out and forms a eutectic with the $SnCu_3$. It is evident that these alloys possess much the same features as the other antifriction alloys, viz. particles of a hard compound embedded in a softer matrix. In the copper-tin alloys, however, the matrix is a solid solution of tin in copper and is very much harder than the tin and lead alloys, and it follows that the plasticity of the copper alloys is very inferior to that of the true antifriction alloys.

Charpy gives the following results of compression tests on some of the copper-tin alloys, together with their analyses. A compression of 7·5 mm., as in the tests on the other alloys already quoted, was not practicable on account of the greater hardness of the alloys, but comparative results were obtained by measuring the compression produced by a load of 5000 kilograms.

No. of Alloy.	Composition.						Load corresponding to a Compression of 0·2 mm.	Compression produced by a Load of 5000 kgs.
	Cu.	Sn.	Pb.	Sb.	P.	Zn.	Kilograms.	Millimetres.
1	89·15	9·05	[illegible]	0·25	[illegible]	0·11	1925	3·7
2	88·55	10·32	0·25	0·13	0·223	0·10	2100	3·1
3	86·79	11·20	0·41	0·51	0·11	1·17	2350	3·2
4	85·70	12·15	0·51	0·12	0·385	0·84	3000	2·7
5	84·83	13·11	0·38	0·13	0·16	0·59	3100	2·4
6	84·30	14·60	0·10	0·10	0·215	0·56	3600	1·9
7	80·65	19·18	0·01	0·21	[illegible]	.	5000	1·4

Alloys of Group IV. Alloys of copper and tin containing relatively large quantities of lead have recently been largely used as antifriction metals, and are frequently known as *plastic bronzes*. The lead, which may reach as much as 30 per cent., does not alloy with the copper, but separates out in the form of globules, which ought, if the alloy is properly mixed and cast, to be uniformly distributed throughout the mass of the alloy. The constitution of these alloys differs somewhat from other antifriction alloys, for, instead of hard particles embedded in a soft matrix, we have soft particles embedded in a comparatively hard matrix. The addition of lead increases the plasticity of the bronze, as is shown by Charpy's compression tests given below.

No. of Alloy	Composition						Load corresponding to a Compression of 0·2 mm.	Compression produced by a Load of 5000 kg.
	Cu	Sn	Pb	Sb	P	Zn		
							Kilograms	M.M.
1	[illegible]	6·60	8·44	0·16		0·1[illegible]	1,[illegible]0	1·8
2	80·[illegible]5	2·2[illegible]	1[illegible]·[illegible]6	2·67	0·[illegible]1	0·60	1,00[illegible]	1·8
3	84·70	10·05	4·0[illegible]	0·14	0·11	0·46	[illegible]	[illegible]
4	82·30	8·98	7·2[illegible]	0·14	0·39	0·10	2,000	2·4

In addition to the ordinary lead bronzes there are the bronzes containing phosphorus and those containing nickel. The addition of phosphorus introduces the hard compound Cu_3P, and, although comparative data are lacking, it seems probable that the presence of this constituent has an important influence on the properties of the bronze.

Photograph 19 shows a phosphor-bronze containing lead, unetched. The hard compounds $SnCu_4$ and PCu_3 can be distinctly seen standing in relief, but most of the lead has been torn out in the process of polishing, leaving pits which appear as black dots in the photograph.

The addition of a small quantity of nickel is said to enable a larger amount of lead to be added to the bronze without causing segregation. These bronzes are now largely used in America, and contain as much as 30 per cent. of lead and 1 per cent. of nickel. The part played by the nickel has not been fully explained.

In addition to the alloys already dealt with, there are certain alloys of zinc, tin, and antimony, which are used for special purposes, and also alloys of lead, copper, and antimony, which are occasionally employed as antifriction metals. The alloys of zinc, tin, and antimony possess a high compressive strength, as shown by Charpy's figures given in the table (p. 252), and they are employed for bearings of machinery, such as rock-breakers, where strength is of more importance than perfect antifrictional qualities.

No. of Alloy.	Composition.			Load corresponding to a Compression of 0·2 mm.	Load corresponding to a Compression of 7·5 mm.
	Zinc.	Antimony.	Tin.		
				Kilograms.	Kilograms.
1	100	...	...	500	4200
2	90	10	.	2450	Broke at 5000
3	80	20		3000	,, 4000
4	70	30		4100	,, 4700
5	90	5	5	1100	3950
6	80	10	10	1350	4150
7	70	15	15	1800	5200
8	80	5	15	1120	3550
9	70	7 5	22·5	1225	3500
10	60	10	30	1240	3350
11	90	...	10	750	3050
12	80	..	20	850	2725
13	70		30	850	2500
14	60	...	40	575	2175

Zinc and tin do not unite to form definite compounds, but zinc and antimony combine to form a hard compound, which Charpy describes as an antimonide of zinc

The useful alloys are those rich in zinc, in which the hard compound is the first to solidify.

The alloys of lead, copper, and antimony have characteristics similar to the other antifriction alloys The copper unites with the antimony to form the hard violet coloured compound $SbCu_2$, part of which crystallises in needles and the remainder enters into the composition of the eutectic. The alloys should contain from 15 to 25 per cent. of antimony and not more than 10 per cent. of copper. The results of some compressive tests on these alloys are given by way of comparison (p. 253).

Alloys of aluminium have from time to time been suggested for use as bearing metals, and it is said that the Northern Railway of France uses an alloy of 92 per cent. aluminium and 8 per cent. copper for carriage and waggon bearings with excellent results. Hughes, however, states that experiments with this alloy carried out on the Lancashire and Yorkshire Railway have not proved satisfactory, the metal proving hard and brittle, and considerable labour being involved in properly bedding the bearings to the journals.

No. of Alloy.	Composition.			Load corresponding to a Compression of 0·2 mm.	Load corresponding to a Compression of 7·5 mm
	Lead.	Copper.	Antimony		
				Kilograms.	Kilograms
1	66·6		33·4	750	1250
2	66·6	12·9	20·5	1120	1325
3	66·6	23·2	10·2	350	850
4	80	7·75	12·25	730	1525
5	80	13·9	6·1	200	800
6	80		20	640	1400
7	90	3·8	6·2	110	1325
8	90	6·9	3·1	190	800
9	90		10	610	1400
10	100		...	80	550

Aluminium to the extent of 5 per cent is sometimes added to the zinc alloys and adds considerably to their hardness

As regards the relative merits of white metal and bronze bearings it is frequently stated that white metal is superior, and some writers have brought forward experimental evidence to prove their statements

Charpy says that bronzes appear to be inferior to white metals on account of their lack of plasticity and their tendency to cutting; and in connection with railway axle bearings the same opinion has been expressed, as already mentioned, by Mr Salomon and Mr Chabal. On the other hand, Mr Clamer states that railway engineers only recognise two alloys as standard, viz. phosphor-bronze containing lead, and ordinary bronze containing lead. General comparisons are always dangerous and frequently misleading, and the truth of the matter would seem to be that white metals and bronzes each have their particular uses for which they are best adapted. In cases where accuracy of adjustment is impossible, as in the case of a long shaft requiring several bearings, or where variable forces come into play with a tendency to irregular wear, as in the case of railway bearings, the plasticity of white metal is an invaluable property. On the other hand, where accuracy of adjustment is possible and the rotary motion regular, plasticity is of secondary importance, and bronzes give results in practice which leave nothing to be desired.

ALLOYS OF TIN, COPPER, AND ANTIMONY.

Composition			References and Remarks.
Tin	Copper.	Antimony.	
96	4	8	Thurston. Ordinary bearings.
90	2	8	Thurston. Russian railroads for car bearings.
88·8	3·7	7·4	Thurston. Karmarsch metal
87	6	7	Hiorns. For heavily loaded bearings
85	5	10	Ledebur. Jacoby metal. Admiralty lining metal.
85	7·5	7·5	German Navy.
83·33	5·55	11·11	Used for car bearings on French railroads.
83	8	9	Admiralty for heavy load.
83	6	11	Ledebur. Used by Berlin railroads
82	4	14	Motor bearings, Lancashire and Yorkshire Railway electrical rolling stock
82	6	12	Ledebur Used by Orleans and the Western Austrian railroads.
82	8	10	Bearings for valve rods and eccentric collars.
80	10	10	Thurston Used by Swiss railroads. Also Lancashire and Yorkshire Railway for loco. coupling rod bushes, crossheads, etc.
78·5	10	11·5	Thurston Used by Russian railroads
78	10	12	Daimler Co. Lining of bearings of crank-shafts and connecting-rods of motor buses.
71	5	24	Thurston standard white metal Used for packing of valves and eccentric collars.
67	22	11	Thurston. Used by Great Western Railway.
67	11	22	Used by French state railroads

ALLOYS OF LEAD, TIN, AND ANTIMONY.

Composition.			References and Remarks.
Lead.	Tin.	Antimony.	
80	12	8	Used by Eastern railroad (France) for metallic packings
77·7	5·9	16·8	Quoted by Thurston as being the composition of Magnolia and Tandem metals.
76	14	10	Used for metallic packings by the Orleans and Paris L M. railroads.
73	12	15	Used by Northern Co. (France) for metallic packing of piston-rods.
73·5	8	18·5	Campbell. American railways
70	20	10	Metallic packings of eccentric collars. French state railroads.
70	15	15	Lancashire and Yorkshire Railway carriage and waggon bearings
68	15	17	"Graphite" metal analysed by Dudley.
68	21	11	Campbell. American railways.
60	20	20	Ledebur Railroad bearings
42	46	12	Hiorns. Hoyles metal
42	42	16	Ledebur. Journal boxes French state railroads.
37	38	25	Thurston Italian railroad companies.

Alloys of Copper and Tin containing Zinc, Phosphorus, etc.

Composition.					References and Remarks.
Copper.	Tin.	Zinc.	P.	As.	
86	14		...		Thurston. Locomotive bearings.
82	18				Ledebur. Car bearings of "Compagnie du Nord"
84	14	2			Used by French state railroads for pieces subjected to alternating friction
82	16	2			Used by French state railroads for pieces subjected to circular friction.
80	18	2	...		Thurston. Lafond alloy
58	28	14	..		Thurston. Margraff alloy.
56	28	16			Thurston. Fenton alloy.
89	10			0·8	Dudley. Arsenic bronze.
85·7	12·2		0·4		Charpy. Phosphor-bronze.
84·8	13·4		0·16		Charpy. Phosphor bronze.
88·7	9·5	...	0·7		Law. Phosphor-bronze.
87·6	10·8	...	1·0		Law. Phosphor bronze.

Bronzes containing Lead

Composition.						References and Remarks.
Copper	Tin	Lead	P	As.	Ni	
79·7	10	9·6	0·8			Dudley's "standard" phosphor bronze
77	8	15				Dudley's "alloy B"
84·5	10	5	0·5	...		Slide valves, Lancashire and Yorkshire Railway.
83·3	6·6	8·4	...	...		Charpy.
80·5	2·2	10·8	0·2			Charpy.
80	5	15	...			Ordinary axle box bearings, Lancashire and Yorkshire Railway.
82·3	8·9	7·2	0·4			Charpy.
75·4	9·7	14·5	...		...	Carbon bronze analysed by Dudley.
78·5	9·2	15·0		...	...	Graney bronze ,, ,,
76·4	10·6	12·5		...		Damar bronze ,, ,,
81·2	10·9	7·2	0·4			Ajax bronze ,, ,,
79·2	10·2	9·6	0·9	...		Phosphor-bronze ,, ,,
76·8	8	15	0·2		...	B. metal. Car bearings of the Pennsylvania railroad.
82·2	10·0	7·0		0·8		Dudley. Arsenic-bronze B.
79·7	10·0	9·5	...	0·8		,, ,, C.
64	5	30	...	...	1	Plastic bronze used on many railways for heavy bearings

MISCELLANEOUS ALLOYS.

Composition.						References and Remarks
Cu	Sn	Pb.	Zn	Sb	Fe.	
5		...	85	10		Ledebur.
70·2	4·2	14·7	10·2		0·5	Camelia metal analysed by Dudley.
4·0	9·9	1·1	85·5			Salge ,, ,, ,,
92·4	2·4	5·1	...	..	0·1	Delta ,, ,, ,,
59·0	2·1	0·3	38·4		0·1	Tobin bronze ,, ,,
55·7	0·9	...	42·6		0·7	Harrington bronze ,, ,,
6	14	...	80		...	Thurston. Fenton alloy.
5·5	17·5		77			Ledebur.
5	65	..	30	...	.	Campbell. Parsons white brass.
1·4	70	.	29·6			Admiralty metal for work under water
5	10		85			Campbell.
2	8	75	..	15		Used on several railways. These alloys are harder than the simple lead alloys but will not stand reversals of motion.
3	11·5	72	.	13·5		
2	51	37		10		
10	...		85	..		Al 5. Lumen bearing metal.
12			82			Al 6 Special ,, ,,
76	3	1	20	. .	.	Daimler motor-bus bearing brasses.

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CHAPTER XIII.

ALUMINIUM ALLOYS.

WITH the introduction of electrical methods of reducing aluminium, and the consequent production of the metal in quantities and at a price sufficiently low to bring it within the sphere of practical utility, attention was directed to the alloys of aluminium with the object of finding light alloys which would be stronger and more easily worked than the pure metal These attempts, however, have not met with very marked success, and few of the light aluminium alloys have proved of any industrial value. The reason of this is to be found in the fact that aluminium unites with most of the common metals to form definite chemical compounds which crystallise out in a matrix of practically pure aluminium, and we know that alloys with conglomerate structures of this description are only useful in special cases. Such compounds are formed with iron, copper, nickel, antimony, manganese, and tin. Zinc, on the other hand, forms solid solutions with aluminium, and the alloys of these metals, either alone or more often with small additions of other metals such as copper or magnesium, are practically the only ones of industrial importance.

Alloys of Aluminium and Zinc. The constitution of these alloys has been studied by Heycock and Neville, Shepherd, and more recently by Rosenhain and Archbutt, whose equilibrium diagram for the complete series of alloys is reproduced in fig. 67. The microscopical examination of the alloys confirms the evidence of the equilibrium diagram that at one end of the series the alloys containing less than 40 per cent. of zinc are single homogeneous solid solutions, and they are therefore the only ones of practical importance. Those containing up to 15 per cent. of zinc are soft enough to be rolled or drawn, while beyond this amount the alloys are hard and more suitable for castings, as they are easily worked. It is only within recent years that the price of aluminium has enabled its alloys to be used on a large scale, but the importance of the alloys with zinc has long been recognised, and for many years they have been employed in the construction of scientific instruments where lightness is a consideration. One of these alloys has been manufactured for many years by Carl Zeiss of Jena, and is known under the name of Ziskon. Cast in sand, it has a specific gravity of 3·4 and an ultimate tensile strength of 11 tons per sq. in. and is largely used for parts of scientific instruments where lightness and a considerable degree of strength are required. As regards its hardness and the ease with which it can be worked it is somewhat similar to bronze.

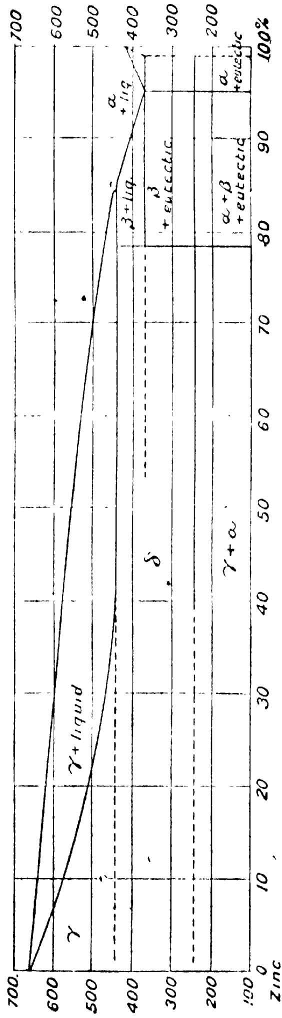

FIG. 67.—Equilibrium Diagram of Aluminium-zinc Alloys.

A soft alloy with properties similar to that of brass as regards working is also made by Zeiss of Jena, and is known under the name of Zisium. This alloy contains a very much smaller percentage of zinc, together with small quantities of tin and copper. It is lighter than Ziskon, having a specific gravity of 2·95, but has a tensile strength less than half that of Ziskon, viz. 5 tons per sq in. Perfect screw threads can be cut on the alloy, and it is used in parts of instruments where a certain amount of ductility rather than strength is desirable.

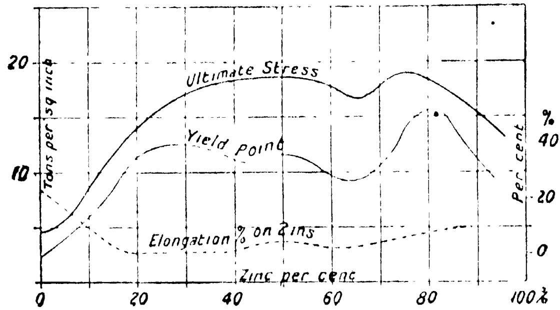

FIG. 68.—Tensile Tests on Sand Castings.

The mechanical properties of the pure aluminium-zinc alloys have been investigated at some length by Rosenhain and Archbutt, and the results of their tensile tests are given in the accompanying curves. Fig. 68 gives the results of tensile tests on sand castings, and fig. 69 the corresponding tests on chill castings Fig. 70

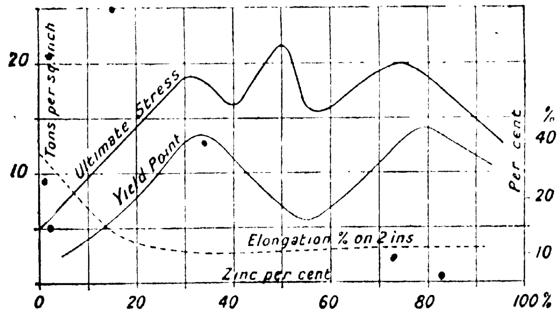

FIG. 69.—Tensile Tests on Chill Castings.

shows the curves representing tests on hot-rolled bars 1¼ ins. in diameter of the alloys containing up to 26 per cent. of zinc, and fig. 71 the results of tests on cold drawn bars $\frac{18}{16}$ ins. in diameter.

With more than 25 per cent. of zinc the alloys are extremely hard and difficult to roll. It is, however, in the form of castings that these alloys are principally employed, and the motor industry accounts for a large proportion of the total output. For this purpose the percentage of zinc seldom exceeds 20 per cent, and by far the largest quantity of castings made contain about 10 per cent. of zinc. A small quantity—2 or 3 per cent.—of copper is usually added, as it improves the working qualities of the metal. A common mixture for gear cases, etc., of motors contains approximately 88 per cent. of aluminium, 10 per cent. of zinc, and 2 per cent. of copper, and has a tensile strength of 8 to 10 tons per sq. in.

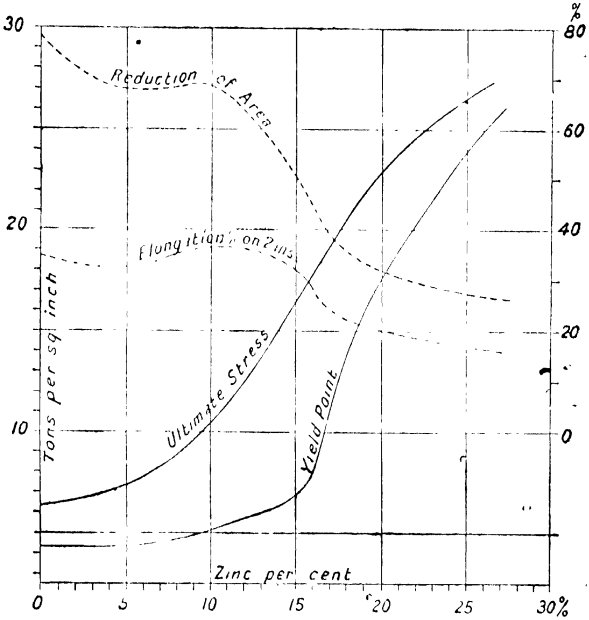

FIG. 70.—Tensile Tests on Hot-rolled Bars 1¼ ins diameter.

The alloys of aluminium and zinc exhibit the phenomenon, common to most of the aluminium alloys, of ageing. Although much less marked than in many of the alloys, it is, however, noticeable that whereas a fresh casting is difficult to machine owing to the metal "dragging," the same casting after the lapse of a few weeks can be machined as easily as brass. The change appears to be accompanied by a slight increase in the tensile strength of the metal, but there is no tendency towards disintegration as shown by many of the alloys of aluminium with other metals.

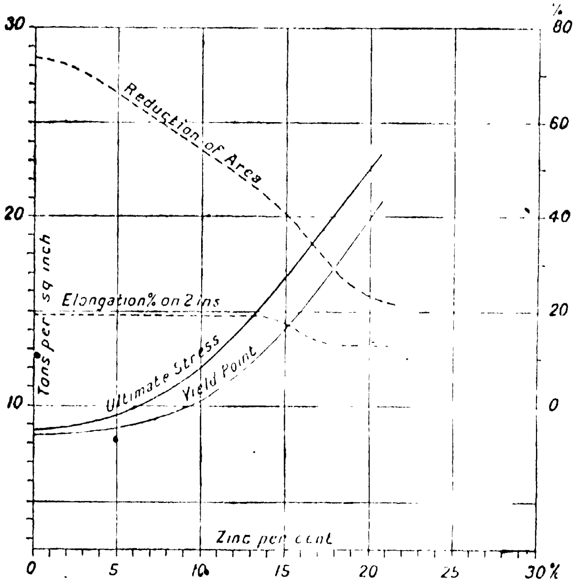

FIG. 71.—Tensile Tests on Cold drawn Bars 1⅛ in. diameter

Magnalium.[1]—Alloys of aluminium and magnesium were prepared by Wohler as long ago as 1866, and by Parkinson in 1867. The latter observes that "none of the magnesium-aluminium alloys promise any practical service in the arts."

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[1] Patented 1898, No. 24,878.

Unfortunately, both these experimenters appear to have chosen alloys with high percentages of both metals, and it was left to Dr Mach to discover that small percentages of magnesium improve to a very marked degree the mechanical properties of aluminium. Dr Mach experimented on alloys containing 10 per cent. of magnesium; but magnesium is an expensive metal, and, as a matter of fact, commercial magnalium contains very much less than this amount. The cost of an alloy containing 10 per cent. of magnesium would be, for all ordinary purposes, prohibitive.

Boudouard has determined the freezing-points of the aluminium-magnesium series, and his results indicate the existence of two compounds corresponding to the formulæ AlMg and $AlMg_2$. The existence of these compounds is confirmed by the microscopical examination, and they have also been isolated by chemical means; but it is interesting to note that the microscopical examination reveals another compound corresponding to the formula Al_4Mg, which has also been isolated by chemical means, although its existence is not even suggested by the freezing-point curve. It may be that this is yet another example of mutual solubility or isomorphism of a compound with a metal.

As regards the general properties of the alloys, those containing more than 15 per cent. of magnesium at one end of the series and those containing more than 15 per cent. of aluminium at the other, are all brittle, the maximum brittleness being reached with the alloy containing 50 per cent. of each metal, which can be crushed between the fingers.

It has already been stated that commercial magnalium contains only a small percentage of magnesium, and, although a large number of alloys are manufactured and sold under the name of magnalium, few of these, if any, appear to contain more than 2 per cent. On the other hand, they all contain a variety of other metals, more especially copper, tin, nickel, and lead.

The importance of magnesium as a deoxidiser must not be overlooked, for it is even more readily oxidised than aluminium; and its beneficial influence on aluminium is in no small degree due to its power of freeing that metal from dissolved oxide.

The three magnalium alloys most commonly used in this country are described by the makers as X, Y, and Z. Of these, X is intended solely for castings where strength is of primary importance, Y is used for ordinary castings, and Z is intended for rolling and drawing.

As regards alloy X it has been stated by Barnett that it contains 1·76 per cent copper, 1·16 per cent nickel, 1·60 per cent magnesium, and small quantities of antimony and iron. Photographs 36 and 37 show the microstructure of this alloy.

Alloy Y is somewhat similar in composition, except that it contains no nickel, but small quantities of tin and lead

Alloy Z contains 3·15 per cent of tin, 0·21 per cent. of copper, 0·72 per cent of lead, and 1·58 per cent of magnesium

The tensile strength of ordinary castings with alloy Y varies from 8½ to 10 tons per sq in, and that of rolled samples of alloy Z varies from 14 to 21 tons per sq in

The alloys work well, and excellent screw-threads can be cut. The speed of working is about the same as that of brass, and the tools should be lubricated with turpentine, vaseline, or petroleum. Alloy Z is exceedingly ductile, and can be spun and drawn into the finest wires. For these operations vaseline or a mixture of 1 part stearine and 4 parts turpentine has been found suitable. In drawing tubes or wire the alloy must be annealed by heating and cooling suddenly Slow cooling produces hardening.

For rolling, magnalium should be heated to a temperature of 350°, and the temperature of the rolls kept at about 100°. Annealing should take place after every second pass.

With reference to the influence of heat treatment on these alloys it is of some interest to note that although quenching has the effect of softening them, the softening is not permanent. It is followed by a gradual hardening which may continue for several hours before the maximum hardness is reached.

With regard to the casting of alloys X and Y, the metal should be melted at as low a temperature as possible (about 660°) under a layer of charcoal, and the scum carefully removed before pouring In making the mould the sand should not be rammed so closely as for brass castings, and it is recommended to mix the sand with a tenth part of meal in order to allow free escape of gases. The facing of the mould should be treated with blacklead, French chalk, or petroleum and lycopodium powder Metal moulds are also suitable, if polished with blacklead

Magnalium contracts considerably on cooling (from 2 to 4 per cent.), and to insure good castings it is necessary to have a good head of metal and large gates and runners.

Magnalium can be soldered, but the operation is difficult on account of the high conductivity for heat of the alloy as well as the difficulty of obtaining a surface free from a film of oxide.

In a paper read before the American Society of Automobile Engineers, Mr Morris Machol recommends the use of magnalium for the cylinders and pistons of petrol motors. He claims that the alloy is sufficiently strong and has the additional advantages of light weight, low coefficient of friction, and high thermal conductivity which prevents over-heating.

Magnalium is very little affected by dilute acids, and can be employed with perfect safety for the manufacture of cooking utensils and all culinary appliances.

It is evident that magnalium is eminently suitable for a great variety of purposes, and there is no doubt that its price alone prevents it being more widely used.

Aluminium-Copper.—Alloys of aluminium and copper are used to some extent; but only those containing small percentages of copper are of any industrial value. These alloys have been used in naval construction, particularly in France; and in 1894 a torpedo-boat was built in this country by Messrs Yarrow and Co. for the French navy, in which the hull was composed of an alloy containing 94 per cent. of aluminium and 6 per cent. of copper. The excessive corrosion of this alloy by sea-water, however, has effectually prevented any further trials. In the automobile industry alloys containing 3 to 5 per cent. of copper are sometimes used.

With regard to the constitution of the alloys, the equilibrium diagram of the entire series has been given in fig. 56, and it is only necessary to say that the addition of copper to aluminium gives rise to a hard eutectic consisting of aluminium and the compound Al_2Cu, which freezes at a temperature slightly below 550° and separates between the crystals of pure, or practically pure, aluminium. The compressive strength is therefore increased, and the alloys are more easily worked than pure aluminium.

The curves in figs 72, 73, and 74 are plotted from the results

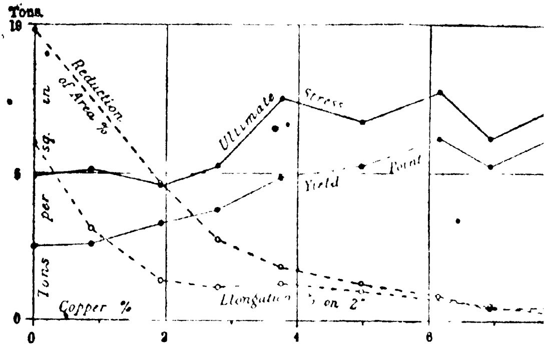

FIG. 72.—Tensile Tests on Sand Castings

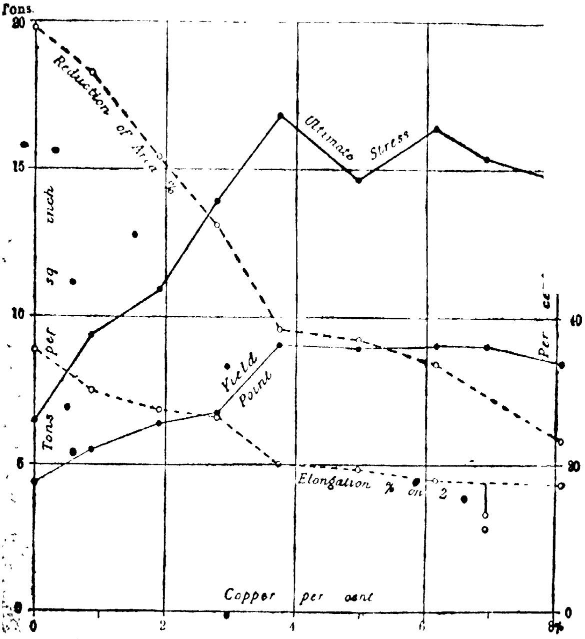

FIG. 73.—Tensile Tests on Bars rolled down to 1¼ in diameter.

of tests by Carpenter and Edwards and show the mechanical properties of the alloys in the form of sand castings, rolled bars, and cold-drawn bars respectively. From these results it is evident that there is no advantage in adding more than 4 per cent. of copper, as beyond this point there is a decrease in ductility without any corresponding increase in tenacity. The alloys do not contract on cooling more than aluminium, and they appear to be practically unaffected by heat treatment below the melting-point of the eutectic. Figs. 75, 76, and 77 show the results of tests on chill castings and also on sand castings slowly cooled and quenched from 450°.

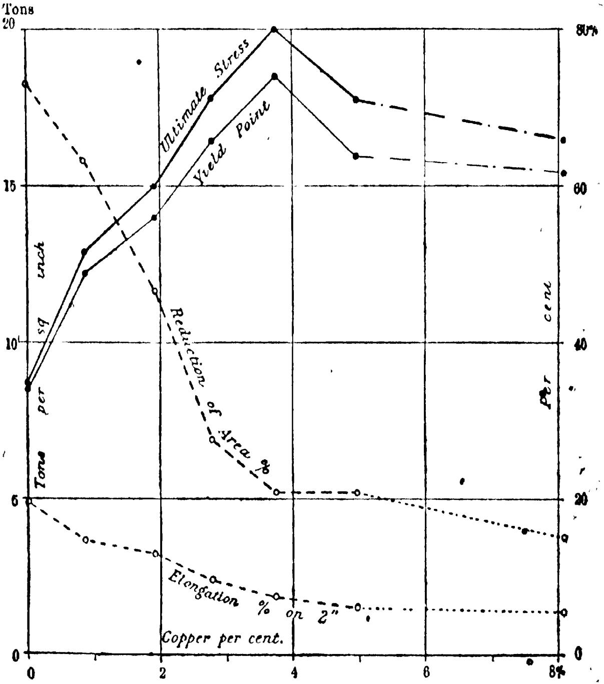

Fig. 74.—Tensile Tests on Bars Cold-drawn.

An alloy under the name of Partinium has been found on analysis to contain aluminium 88·48, copper 7·36, zinc 1·67 silicon 1·14, and iron 1·31 per cent.

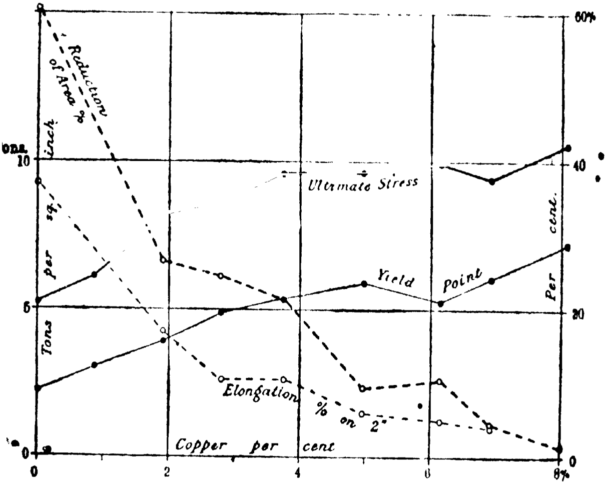

FIG. 75.—Tensile Tests on Chill Castings.

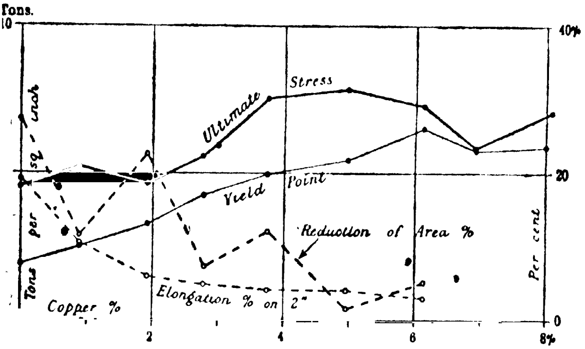

FIG. 76.—Tensile Tests on Sand Castings, slowly cooled from 450° C.

Aluminium and Nickel.—Nickel is sometimes added to aluminium as a hardening agent in place of copper. It is unnecessary to consider the constitution of the nickel-aluminium series in detail, as only those alloys at the extreme end of the series are of any practical value. These alloys contain less than 5 per cent. of nickel, and consist of crystallites of a brittle compound, corresponding to the formula $NiAl_6$, embedded in practically pure aluminium.

The effect of nickel on aluminium is therefore very similar to that of copper. Occasionally nickel and copper are both added to aluminium, but it is doubtful whether any advantage is derived from this procedure.

The tendency at the present time is to use complex alloys containing small percentages of several metals rather than simple binary alloys. One of these complex alloys which has attracted a good deal of attention is known under the name of Duralumin, and is said to contain 3·5 to 5·5 per cent. of copper, 0·5 to 0·8 per cent. of manganese, and 0·5 per cent. of magnesium. An actual analysis of a sample gave 4·06 per cent. copper, 0·53 per cent. manganese, 0·86 per cent. magnesium, 0·40 per cent. silicon, and 1·55 per cent. iron.

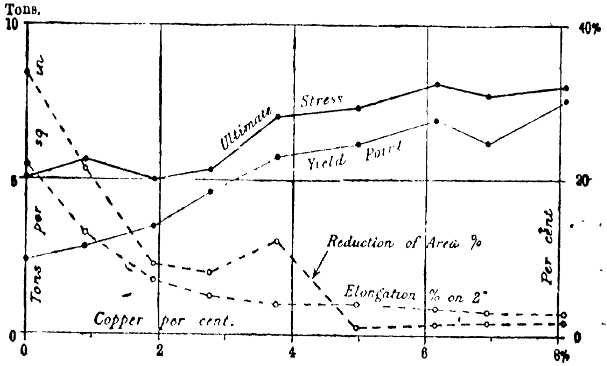

FIG. 77.—Tensile Tests on Sand Castings, quenched in Water from 450° C.

The annealed alloy has a specific gravity of 2·79, and a tensile strength of over 16 tons per sq. in., with 17 per cent. elongation on 2 ins. In the form of thin sheet obtained by cold rolling the tensile strength reaches as much as 34 tons per sq. in., with an elongation of 3 per cent. In addition to the hardness imparted by cold working, duralumin may also be hardened by heat treatment. If the alloy is heated to a temperature between 410° and 500° and quenched it remains soft, but subsequently hardens, as already mentioned in the case of the aluminium-magnesium alloys. The maximum hardness is reached after the lapse of about forty eight hours. By this means the alloy has been obtained with a tensile strength of nearly 40 tons per sq. in.

The hardness obtained by heat treatment, however, is to some extent removed at comparatively low temperatures, and this must be taken into account in the practical applications of the alloy. For example, Lantsberry states that a sample of sheet which broke at 29·4 tons per sq. in. was boiled in water for four hours and was then observed to break under a load of 26·1 tons. After annealing for half an hour at 260° this was further reduced to 22·9 tons.

From what has been said of the ageing, or slow change, taking place in aluminium alloys it is evident that this property is intimately connected with the aluminium itself, the metal with which it is alloyed merely serving to retard or accentuate the change. For example, the alloys of aluminium with iron, nickel, cobalt, manganese, etc., in which these metals are present in relatively high percentages—usually from 25 to 50 per cent.—will, in the course of time, disintegrate and fall to pieces without the application of any external force. It is probably the same change which causes the hardening already noticed in the industrial alloys.

The author has suggested that this alteration in properties is probably due to an allotropic change in the aluminium induced by the presence of impurities, and there appears to be some ground for this belief. Cooling curves of aluminium to which small quantities of metallic impurities have been added show a decided evolution of heat towards the end of solidification which is not due to the solidification of a eutectic, is not proportional to the amount of impurity added, and occurs at a constant temperature. Moreover, Turner and Murray have shown that aluminium expands on solidification, a property which, although not necessarily proving an allotropic change, at least indicates a molecular rearrangement. Whether it will ever be possible completely to control these changes remains to be seen, but the introduction of such alloys as duralumin appears to be a step in the right direction.

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CHAPTER XIV.

SILVER AND GOLD ALLOYS.

Silver Alloys.

The alloys of silver with copper may alone be said to have any important industrial applications. From time to time many other silver alloys have been suggested; but none of them have taken the place of the well-known silver-copper alloys. The importance of these alloys may be realised when it is remembered that the average weight of standard silver articles, hall-marked at the Assay Offices of Birmingham, Sheffield, and Chester alone, during the last five years amounts to 6,037,214 oz., or nearly 225 tons; and it has been estimated that the amount of standard silver melted annually in the United Kingdom is close on 700 tons.

The constitution of the silver-copper alloys has been thoroughly investigated by Roberts-Austen and Heycock and Neville, and the results of their researches are plotted in the freezing-point curve shown in fig. 78.* It will be seen that the metals form a simple series of alloys with a eutectic containing 71·9 per cent. of silver and melting at 778°. This is the alloy which Levol in 1854 considered to be a definite compound on account of its remarkable homogeneity.

The alloys of industrial importance are few in number, and contain not less than 80 per cent. of silver. The following table shows the composition of the silver standards used for coin and for plate in different countries:—

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* The extent of the line representing the eutectic has not been accurately determined, but it should be much longer than that shown in the diagram.

SILVER STANDARDS.

Country.	Coinage.		Plate.
	Denomination.	Fineness.	Fineness.
Austria-Hungary	5 crowns	900	950
,, ,,	1 crown	835	900
,, ,,	Thaler	833½	800
,, ,,	.	..	750
Belgium	5 francs	900	900
,,	2 and 1 franc and 50 centimes	835	800
Bolivia	1 boliviano	900	...
Brazil	2 milreis	916·6	...
Bulgaria	21 lew	835	...
Chili	1 peso	900	
Denmark	Crown	800	826
Egypt	10 Piastres	900	..
France	5 francs	900	950
,,	Others	835	850
Germany	Marks	900	800
Greece	5 drachmas	900	
,,	Others	835	
Great Britain	All	925	925
,,		...	959
British Colonies—			
Canada and Newfoundland	50 cents	925	...
Australasia	Shilling, etc.	925	...
Hong Kong & Straits Settlements	Cents	800	
Holland	Florin	945	934
,,	.	...	833
India (Burma, Ceylon, and Mauritius)	Rupee	916·6	...
Italy	5 liras	900	950
,,	..	...	900
,,	...	...	800
Japan	Yen	900	...
Mexico	Peso	902·7	...
Norway	Kroner	800	828·1
,,	50 ore	600	...
Peru	Sol	900	.
Portugal	5 testoons	916·6	916·6
,,	.	...	833
,,	..		800
Roumania	5 leys	900	...
Russia	Rouble	900	947·9
,,	Kopecks	500	916·7
,,	...	...	875·0
Servia	5 dinars	900	...
Spain	5 pesetas	900	916·6
,,	2, 1, and 1½ peseta	835	750
Sweden	2 and 1 kroner	800	828·1
,,	50 ore	600	...
Switzerland	5 francs	900	875
,,	2, 1, and ½ franc	835	800
Turkey	20 piastres	900	900
United States	All	900	...

It will be seen that an alloy containing 90 per cent. or 900 parts of silver per thousand is most generally adopted, while the British standard contains 92·5 per cent. or 925 parts per thousand. It should be mentioned that the composition of silver and gold alloys is seldom expressed in percentages, but in parts per thousand. Thus an alloy of "925 fine" signifies an alloy containing 925 parts of fine or pure silver per thousand.

Sterling silver was first defined by a statute of Edward I., and must contain 11 oz. 2 dwt. of fine silver and 18 dwt. of copper to the pound. The word "sterling" was apparently derived from the Easterlings, or workmen who came from Germany, and who were the first to make and work the alloy in this country. Stow says in his *Survey of London*, published in 1603: "But the money of England was called of the workers thereof, and so the Easterling pence took their name of the Easterlings, which did first make this money in England in the reign of Henry II., and thus I set it down according to my reading in Antiquitie of money matters, omitting the imaginations of late writers, of whom some have said Easterling money to take that name of a starre stamped on the border or ring of the penie: other some, of a bird called a stare or starling stamped on the circumference, and others (more unlikely) of being coined at Stiruelin or Starling, a towne in Scotland."

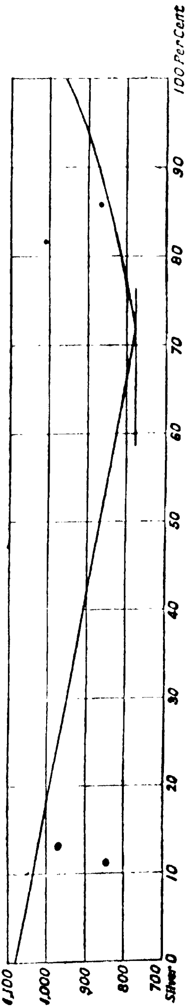

FIG. 78.—Freezing-point Curve of silver-copper Alloys

The history of the coinage standard has been well described by Roberts-Austen, and we cannot do better than quote his own words:—

"Anglo-Saxon and Anglo-Norman coins are believed to have been of the 'old standard' 925, and a coin of William the Conqueror which I assayed proved to be 922·8. In England this old standard appears to have remained unchanged until the thirty-fourth year of King Henry VIII., when a great fall took place. A still deeper fall in the standard fineness ensued in 1545, and again in 1546, and in the reign of Edward VI. It fell to its lowest point in the fourth year of the latter monarch, when the pound of silver contained only 3 oz. of fine silver and 9 oz. of base metal, that is, the standard, expressed decimally, was only 250. Strangely enough, this base coinage was projected with a view to secure by the transaction the sum of £160,000, to be devoted to the restoration of the standard generally. Half this sum appears to have been actually obtained. As a step to the withdrawal of the base money, it was almost universally decried, that is, the coin which had been current at rates far above its intrinsic value, was officially reduced to a value nearly corresponding with its standard of fineness. Dreadful distress was caused to the people, and the saddest pictures are drawn of the financial condition of England at the time. In 1552 the standard was restored to nearly its original richness, as coins containing 11 oz. 1 dwt. of pure metal and 19 dwt. of base metal, or standard 921, were issued, and this alloy was maintained by Queen Mary. Queen Elizabeth further contributed to the restoration and maintenance of the standard fineness of the coin. A proclamation, dated September 27, 1560, stated that 'her Majesty, who, since she came to the throne, never gained anything by the coinage, nor yet ever coined any manner of base monies, for this realm, had begun a coinage of fine money in the Tower of London.' Notwithstanding the Queen's efforts to restore the coinage in England, the coins circulated in Ireland were deplorably low, as the pound only contained 2 oz. 18 dwt. of fine silver, and 9 oz. 2 dwt. of copper (that is, the standard was only 241).

"The restoration of the standard of the silver begun in the reign of King Edward VI. was, however, completed by Queen Elizabeth, and it has not been since debased."

The standard for plate was raised in 1696 to 11 oz. 10 dwt., or 959 fine, in order to prevent the melting of coins for conversion into plate; but the alloy proved less durable and serviceable than the old standard, to which a return was made in 1697. Both these standards are in existence at the present time, but the purer alloy, which is known as Britannia standard from the hall-mark representing the "figure of a woman commonly called Britannia," is seldom used except for very fine work and complicated designs, where its greater softness is an advantage.

The assaying and hall-marking of standard silver is carried out at authorised "Assay Offices" in London, Birmingham, Sheffield, Chester, Edinburgh, Glasgow, and Dublin, and the marks usually found on silver are a Lion Passant indicating the standard of 925, the initials of the maker, the year of assay represented by a letter, and the heraldic arms of the place of assay. The heraldic arms of the different Assay Offices are as follows:—

London—the head of a leopard.

Birmingham—an anchor.

Sheffield—a crown.

Chester—a sword between three garbs.

Edinburgh—a castle, and the standard represented by a thistle.

Glasgow—a tree growing out of a mount, with a bell pendant on the sinister branch, and a bird on the top branch, over the trunk of a tree a salmon in fesse, and in its mouth an annulet. The standard is also represented by a thistle.

Dublin—the standard 925, and place represented by a harp crowned.

Standard silver is harder than the pure metal, but is sufficiently malleable and ductile to be rolled into thin sheets and drawn into fine wire. At the same time it is perfectly white, and takes a fine polish. These properties make it admirably suited to the purposes of coinage. Unlike most of the malleable alloys, however, it is not a homogeneous solid solution, and this is perhaps its greatest drawback, as it is practically impossible to obtain an ingot of uniform composition owing to liquation. This has been a very serious difficulty in the production of the Standard Trial Plates against which the coinage of the country is ultimately tested. As far back as 1781 Jars suggested the use of hot moulds for this purpose, and in 1873 Roberts-Austen obtained a fairly uniform mass by extremely slow cooling. Matthey, in 1894, adopted the method of casting the alloy in the form of thin sheets, and attempts have also been made to cast the alloy at a temperature very slightly above its melting-point. Numberless experiments have been made from time to time, but none of them have proved entirely satisfactory; and the method finally adopted has been to cast an ingot considerably larger than required, which is rolled to the proper thickness and a number of assays made from different parts of the plate. A piece is then cut out of the plate where the assays are practically uniform and of the correct standard. A lack of uniformity is found in all standard silver, although it is, of course, not of so much importance as in a trial plate. For example, a five-shilling piece, whose diameter is almost the width of the fillet from which it is cut, is richer in the centre than at the edges; while with smaller coins, such as a shilling, where two coins are cut in the width of a fillet, the edge corresponding to the centre of the fillet is richer in silver than the other edge which corresponds to the outside of the fillet. In the case of the strips sold for silversmith's work it has been stated that the average difference between the outside and centre varies from ·8 to 1 part per thousand; and where the alloy is to be hall-marked the manufacturers usually add a small quantity of silver to compensate for any irregularity in composition. The result of this is that at the annual examination at the Royal Mint of duplicate samples submitted by the Assay Offices and known as the "Diets," the mean assays show results varying from 4 to 8 parts per thousand above standard.

Standard silver is melted in plumbago crucibles, which are nearly always heated in coke furnaces. The crucibles vary in size, but those used at the Mint hold about 4000 ounces of metal. They will stand a large number of meltings, and are finally broken up and sold to the smelters. Experiments conducted at the Mint have shown that the average temperature of pouring is about 980°, and the temperature the silver "blanks" are annealed at is about 640°. If insufficiently annealed, or annealed at too high a temperature, the metal is liable to crack with mechanical treatment.

In addition to standard silver, a small quantity of alloy 900 fine, which is not hall-marked, is used in Birmingham for jewellery; and it is stated that alloys as low as 600 fine are employed, but the quantity used must be very small.

In America sterling silver is manufactured on a large scale by mills making a speciality of rolling this alloy. The method of manufacture differs in some respects from that operating in this country. The alloy is melted in furnaces fired by oil, which has the advantage of being free from sulphur and producing no ash from which, in the event of accidents, the silver requires to be separated. The furnaces consist of a cast-iron shell lined with firebrick, with a hole at the bottom through which the jet enters at a tangent, so that the flame does not impinge directly upon the crucible. The crucibles used are of graphite and hold about 1200 ounces, half of this being made up of fine silver and shot copper in the calculated proportions, and the other half consisting of scrap. Under ordinary conditions the time required to melt this quantity is about forty minutes. Before pouring, the metal is deoxidised by adding metallic cadmium equal to 0·5 per cent. of the weight of the alloy, which is pushed down under the metal with tongs to prevent it rising to the surface and burning.

The ingot moulds are of the ordinary pattern, consisting of two parts held together by a ring and wedge, and take an ingot 12 ins. long by 10 ins. wide and 1¼ in. thick. After casting, the ingot is cooled in water and the top end is sheared off. It is now trimmed and planed to remove surface defects before rolling.

The rolling takes place in three stages. First, the plate is passed through the breaking-down rolls, in which it receives as heavy a pinch as possible and its thickness is reduced to ⅜ in. The plate is then annealed in a muffle furnace (also oil-fired) and plunged, while still hot, into a pickling bath containing 1 part of sulphuric acid to 16 parts of water, after which it is dried and examined for surface defects, which are removed with a hammer and chisel. After straightening, the plate is then passed through the running-down rolls until its thickness is reduced to No. 10 B. and S. gauge, when it requires a second annealing and pickling. The sheet, which is now 10 or 12 ft. in length, is again examined for surface defects, and is then passed to the finishing rolls; on leaving the rolls it is again annealed, pickled, and dried in sawdust.

Standard silver can be readily soldered, and the alloys used for the purpose are of some importance. They consist of silver and copper with an addition of zinc, usually introduced in the form of brass; and where a very fusible solder is required, tin is sometimes added The composition of a few characteristic solders is given in the following table:—

SILVER SOLDERS

Composition.				Remarks.
Silver.	Copper.	Zinc.	Tin.	
80·0	13·2	6·8	...	Hard solder used for strong joints.
75·0	20·0	5·0	...	Medium solder.
70·0	22·5	7·5	...	,, ,,
69·4	22·1	8·5	...	,, ,,
66·7	33·3	...	...	,, ,, for enamelled work
64·5	22·5	13·0	...	Ordinary solder for plate work.
62·5	30·0	7·5	...	Common solder.
62·5	31·2	6·2	...	Easy solder for chains.
62·5	20·9	16·6		,, ,,
62·5	20·9	10·4	6·2	Quick-running solder.
56·9	27·7	11·5	3·8	Common quick solder.

These solders possess the same characteristics as the lead-tin solders already referred to. There is a considerable range of temperature between the freezing-points of the constituents, with the result that the solder passes through a semi-solid or pasty stage during cooling.

No account of the silver alloys can be regarded as complete which does not make some reference to their use in the art of plating. The first commercial plating process, which was invented by Thomas Bolsover of Sheffield in 1742, developed into an important industry, and it was not until a hundred years later that "Sheffield Plate" was superseded by electro-plate.

Mr E. A. Smith, the Deputy Assay Master of the Sheffield Assay Office, gives the following description of the method of manufacture of Sheffield Plate. "The silver-plating process pursued in the manufacture of old Sheffield Plate consisted in taking an ingot of copper slightly alloyed with brass, and a thinner ingot of silver finer than standard, and placing them in close contact after their surfaces had been scraped clean and even. The silver was then protected by a thin sheet of copper and a sheet of iron outside that. The whole was tightly bound together with iron wire, and the edges brushed with a solution of borax to prevent oxidation in the subsequent heating. The ingot was next very carefully heated in a reverberatory furnace until the silver began to fuse, and was seen to flow at the edges. It was then quickly removed from the furnace, gradually cooled, and when cold cleaned in an acid solution, after which it was scoured with sand and water and rolled out to the desired thickness. For the purposes of manufacture it was cut up and hammered into the required shape by skilled workmen, or stamped in dies, the edges and parts being soldered together at a moderate heat, and finally burnished by hand. In the early days of silver-plating the manufacture of buttons and buckles was an immense industry, and Bolsover at once established a factory in Baker's Hill for the production of these and other small articles, such as snuff-boxes, etc He experienced great difficulty in regard to labour, and at first he, and others who followed him, had to accept the services of itinerant tinkers and such workmen as they could induce to come from London and other places men who speedily realised their importance and exacted their own terms."

"For the first fifty years the copper was plated with silver upon one side only, but Bolsover's apprentice, Joseph Hancock, improved upon the process and plated both sides, at the same time, extending its application to large articles, such as tankards, coffee pots, etc. Tin was at first applied to hide the raw edges of the copper, or brass, but in 1784 George Cadman, in partnership with Samuel Roberts, substituted solid silver edges and mounts, thus not only hiding an obvious disfigurement, but also protecting the parts most exposed to wear. The earliest forms of Sheffield Plate are generally plain and simple in design, but later the designs were pierced like the silver-pierced work of about the middle of the eighteenth century As a general rule, Sheffield Plate simply reproduced the patterns of solid silver in use at the time."

Another process known as "Close-plating" was carried on simultaneously with Sheffield plating, and was used for the plating of steel articles, such as fruit-knives and candle-snuffers, which often accompanied candlesticks and trays of Sheffield

Plate In this process the steel was carefully cleaned and then tinned by dipping into molten tin It was then covered with thin silver foil, which was beaten, or "closed," over every part by careful hammering, and when this was completed a hot soldering iron was pressed over the whole surface, thereby melting the tin, which alloyed with the silver and soldered it to the steel.

Apart from the silver-copper alloys the only silver alloys of any importance are those with cadmium, platinum, and tin.

Silver-cadmium Alloys.—The alloys of silver and cadmium have long been known, and many years ago a company was formed with the object of electro-depositing an alloy of silver and cadmium in place of pure silver on account of its superiority as regards tarnishing. The attempt was unsuccessful for various reasons, but chiefly on account of the difficulty of obtaining a uniform deposit.

In 1904 Rose drew attention to the fact that silver is capable of dissolving cadmium to the extent of 20 per cent. to form a homogeneous solid solution, and he suggested that the standard trial plates might with advantage be replaced by a silver-cadmium alloy on account of its uniformity in composition. Trial plates were therefore made, and it was found that they were perfectly uniform in composition, and that the cadmium in no way interfered with the ordinary methods of assay. Some difficulty was experienced in melting the alloy on account of the volatility of the cadmium, but the method finally adopted was as follows:—Molten silver at as low a temperature as possible was poured on to the melted cadmium covered with charcoal and contained in a large crucible. By this means the loss of cadmium was reduced to about 0·15 per cent. of the weight of the alloy, and was fairly regular. The loss on remelting the alloy only amounted to 0·08 per cent.

Cadmium, however, is not only of use in the preparation of standard trial plates, but in other countries is extensively used in the manufacture of sterling silver, owing to its valuable properties as a deoxidiser. It increases the malleability and ductility, prevents blistering, and is said to improve the whiteness of the alloy. Moreover, an excess of cadmium is not very material, as it alloys perfectly with the metal without injuring its mechanical properties An American authority states that cadmium is used by practically every manufacturer in the United States, and he gives 0·5 per cent. as the usual addition.

Silver-platinum Alloys.—These alloys are used to a limited extent, but are of sufficient importance to demand a brief description.

The preparation of the alloys is somewhat difficult, owing to the high melting-point of the platinum; but the alloying is effected by gradually adding the platinum in the form of sponge to the molten silver, the whole being thoroughly mixed by stirring. The resulting alloy is granulated and remelted to ensure uniformity of composition.

The most important of the silver-platinum alloys are those used by dentists and sold in the form of wire, sheet, and perforated sheet, under the name of *dental alloy*. They are much more durable, and do not blacken so readily as a silver copper alloy. There are in the market two qualities, the first containing 67 per cent. of silver and 33 per cent. of platinum, and the second containing 75 per cent. of silver and 25 per cent. of platinum. The alloys occasionally contain a small quantity of copper.

Silver-platinum alloys are also said to be used by Birmingham jewellers, but it is probable that the advance in the price of platinum has been the means of checking their use. These alloys contain from 2·5 to 35 per cent. of platinum.

An alloy used for soldering platinum consists of 73 per cent. of silver and 27 per cent. of platinum; and an alloy containing 67 per cent. of silver and 33 per cent. of platinum is employed as the standard of electrical resistance.

Alloys of Silver and Tin.—Alloys of these metals are largely used by dentists as the basis of amalgams for stopping teeth. They come into the market in the form of filings or shavings containing from 40 to 60 per cent. of silver, and are mixed with mercury immediately before use. The amalgam thus formed becomes a hard mass within a few hours. Small quantities of other metals, usually gold, platinum or copper, not exceeding 5 per cent., are occasionally added to the alloy in order to improve its quality.

As regards other alloys of silver, those with zinc and aluminium have had some attention devoted to them, but so far they have not attained any degree of industrial importance.

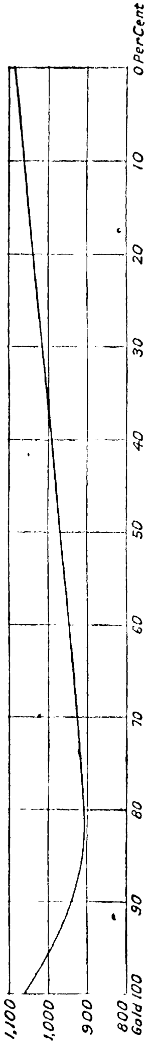

FIG. 79.—Freezing-point Curve of Gold-copper Alloys.

Gold Alloys.

The important alloys of gold are those with copper and silver, and of these the gold-copper alloys are by far the more important, on account of their employment as alloys for coinage.

The constitution of the gold-copper alloys has been studied by Roberts-Austen and Rose, and the freezing point curve of the series as determined by them is shown in fig. 79. It consists of two branches meeting at a point representing the eutectic, which contains 82 per cent. of gold and melts at 905°. The roundness of the curve suggests that the metals are to a considerable extent soluble in one another, and the microscopical examination confirms this view, but the degree of solubility has not yet been ascertained. Standard gold, however, is a homogeneous solid solution of copper in gold, and possesses the crystalline structure of a pure metal. An old-fashioned system of expressing the fineness of gold alloys in "carats" and grains, or "carat grains," is still in use in this country, and requires some explanation. The Arabic word *Kyrat* and the Greek *Keration* appear to be the same, and were applied to beans or seeds which were used as weights. The word seems to have been retained after the introduction of standard weights, for we find a small Greek weight known as a *ceratium*, from which our carat, or "karrett," as it was formerly spelt, is derived. The carat contains 4 grains, and pure gold is taken as 24 carat, so that, to take an example, 18-carat gold contains

$\frac{18}{24}$ of pure gold, or 750 fine. This system was retained in the Mint until 1882, when it was replaced by the decimal or "parts per thousand" system, but it is still commonly employed by jewellers and goldsmiths

In following the history of the gold coinage in this country we must again quote the words of that eminent authority, the late Sir William C. Roberts Austen He begins with the year 1257, "the 41st year of King Henry III, who made a penny of the finest gold, which weighed two sterlings. This, as Ruding points out, is remarkable as the first coinage of gold in the kingdom, and it is extraordinary that it took place at the height of the king's distress for want of money. The next step of importance was taken in 1343, when King Edward III. coined, or projected a coinage of the standard 994·8 (23 carats, 3½ grains, and ½ grain of alloy), which was referred to by later writers as the 'old sterling' or 'right standard' of England, and Lowndes, quoting the Red Book of the Exchequer, says that the ½ grain of alloy might be either of 'silver or copper.' Although these were not, as Stow considered, 'the first coining of gold in England,' the coins of Edward III were of remarkable beauty, and it was asserted that they were struck from gold prepared by occult aid, by the well-known alchemist Raymond Lully, who had a laboratory in the Tower of London. There are, however, chronological difficulties in the way of this explanation of the origin of the precious metal. No further change was made in the standard fineness of the gold coin until the year 1526, when King Henry VIII. introduced a second standard, 916·66 (22 carats), the professed object being to prevent the exportation of the coin to Flanders. The further modification of the standard, which was effected in 1543, was preceded by a kind of scientific research, as the King ordered the officers of the Mint to prepare, whenever they should be so directed by the Privy Council, alloys to the value of one pound in weight, of such fineness as should be devised by the said Council, in order that the general nature of alloys, similar to those used in foreign realms, might the sooner come to his Majesty's knowledge. The standard 916·66 (which is the standard of the alloy used at the present day for the gold coinage of this country) was again issued in 1544. By a subsequent indenture, dated 1545, the gold was brought down to 833·3 (20 carats). King

Edward VI. improved the fineness of the gold currency in 1549, and in 1552 an indenture was made authorising the coinage of gold both of the old standard 994·8 and of the standard 916·66. Queen Mary issued coins of fineness 994·8. Queen Elizabeth struck coins of both standards. The coinage of gold of the 'gold standard' 994·8 was abandoned in the 12th year of King Charles I., and since that time the standard 916·66 has alone been issued. Coins made of the old standard previously to that period continued to be current until the year 1732, when they were withdrawn from circulation by proclamation."

GOLD STANDARDS.

Country.	Denomination.	Fineness.
Austria-Hungary . .	Ducat	986
" " . . .	20 and 10 crowns	900
Belgium	20 and 10 francs	900
Denmark . . .	20 and 10 kroner	900
France	All	900
Germany	All	900
Great Britain . . .	Sovereign	916·6
Holland	Double ducat	983
"	Ducat and 10 florin	900
Italy	All	900
Japan		...
Norway	20, 10, and 5 kroner	900
Portugal	All	916·6
Russia	All	900
Sweden	All	900
United States . .	All	900

From the above table, giving the composition of the gold coinage alloys used in different countries, it will be seen that the standard most generally adopted, viz. 900 fine, is somewhat lower than in this country.

Standard gold is harder than the pure metal, but is extremely malleable and ductile, and admirably suited to the purposes of coinage. Moreover, the alloy being a homogeneous solid solution, there is not the difficulty of preparing standard trial plates of uniform composition as in the case of standard silver.

The melting of standard gold is carried out in plumbago crucibles heated in coke-fired furnaces similar to those used in the melting of standard silver.

Alloys of gold and copper are largely used for jewellery;

those most commonly used and hall marked are 22 carat or 916·6 fine, 18 carat or 750 fine, 15 carat or 624·5 fine, and 9 carat or 375 fine. The first of these, viz. 22 carat, is too soft for hard wear, and is almost exclusively employed for wedding rings and those parts of rings which hold the precious stones and which have to be exceptionally ductile. The alloys of 18 and 15 carat are used in high-class jewellery, and the 9-carat alloy is used for cheap work In addition to these a number of alloys containing silver in addition to the copper are used for jewellery, and in some cases iron is added. An alloy containing 750 of gold and 250 of iron is mentioned by several writers as "blue gold."

Gold-Silver Alloys.

Although the alloys of gold and silver can hardly be said to have any great industrial value, they are of considerable interest from a theoretical point of view It may be mentioned, however, that these alloys are used to some extent in the manufacture of jewellery, the colour being paler than in the case of the corresponding copper alloys. Until comparatively recently the sovereigns struck in Australia at the Sydney Mint were alloyed with silver instead of copper.

The constitution of the gold-silver alloys has received the attention of many metallurgists, and more particularly Gautier, Roberts-Austen, Rose, Erhards and Schertel, who all agree that the metals are isomorphous and form homogeneous solid solutions throughout the whole series of alloys. The freezing-point curve determined by Roberts-Austen and Rose is shown in fig. 80, and it will be noticed that the lowering of the freezing-point of gold by the addition of silver is very slight until 35 per cent. is reached.

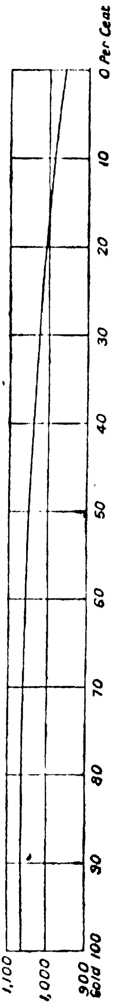

Fig. 80.—Freezing-point Curve of Gold-silver Alloys.

It follows from the constitution of these alloys that they will be uniform in composition, and since 1902 a gold-silver alloy has been used at the Mint for the purpose of assay checks in place of fine gold.

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CHAPTER XV.

IRON ALLOYS.

IN attempting to deal with the alloys of iron our attention is naturally directed to steel, and the question arises, Is steel an alloy? Many years ago Matthiessen declared his belief that steel should be considered as an alloy of iron and carbon, and his opinion has been amply confirmed by modern research. But here we are face to face with another difficulty, for the study of steel has received so much attention, and is in itself so vast a subject, that it would be obviously impossible to compress it into a part of a book on alloys. On the other hand, no book professing to deal with the subject of alloys can possibly ignore the alloys of iron A compromise must therefore be made, and in the following chapter an attempt has been made to deal briefly with the essential facts and to supplement these with a bibliography sufficiently complete to form a reference to the important work dealing with the subject of steel and cast iron.

Iron and Carbon.

The constitution of the alloys of iron and carbon is somewhat complicated by the fact that iron is capable of existing in at least three allotropic modifications; and it is necessary, before dealing with the alloys, to consider the changes which may take place in the iron itself. Roberts-Austen showed that if a cooling curve is taken of the purest iron obtained by electrodeposition, two remarkable irregularities in the curve, due to an evolution of heat in each case, occur at temperatures of 895° and 766°. He considered that these evolutions of heat were due to allotropic changes in the metal, and this view has been supported by the fact that there is a profound change in the physical properties of the metal at these temperatures. Osmond first described the three allotropic modifications as Alpha iron, Beta iron, and Gamma iron, and this nomenclature is now universally adopted. Alpha iron (or α-iron) exists at temperatures below 766°, Beta iron (or β-iron) between 766° and 895°, and Gamma iron (or γ-iron) above 895°.[1]

The physical properties which have received the most attention, and which serve to indicate the molecular changes taking place in iron at different temperatures, are magnetism, dilatation, electrical resistance, and thermoelectric behaviour. These will be referred to later, and it is only necessary to mention here that they fully confirm the existence of three modifications of iron. The crystalline character of the three modifications has also been studied by Osmond, who concludes that they all crystallise in the cubic system, but that while α- and β iron both crystallise in cubes and are capable of forming isomorphous mixtures, γ-iron crystallises in octahedra and does not form isomorphous mixtures with β-iron. Osmond observes that if the allotropy of iron were not conclusively proved by other evidence, it would not be revealed by its crystallography.

If, now, a cooling curve is taken of an iron containing, say, 0·2 per cent. of carbon it will be found that the first evolution of heat is very much less than before, and occurs at a much lower temperature, viz. 825°, while a third evolution of heat is noticed at 690°. Further additions of carbon lower the temperature at which the first evolution of heat takes place, until with 0·37 per cent. of carbon the first two evolutions of heat merge into one at 766°, while the third remains constant at 690°. Still further additions of carbon again lower the temperature at which the first evolution of heat occurs; and when 0 9 per cent. of carbon is reached only one evolution of heat is noticed at 690°. These three evolutions of heat have been named by Osmond A_1, A_2, and A_3; A_1 being the change which occurs at 690° and which is also known as the *recalescence* point; A_2, the change which occurs between 766° in the case of pure iron and 690° in the case of iron containing 0·9 per cent. of carbon; and A_3 the change which occurs between 895° in pure iron and 766° in iron containing

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[1] Many attempts have recently been made to disprove the existence of β-iron, but as yet the evidence has been unsatisfactory and wholly insufficient to support the claims put forward.

0·37 per cent of carbon. The same points are observed on heating steel as well as during cooling, but they do not occur exactly at the same temperatures, and in order to distinguish the points observed during heating or cooling the letters c (chauffant) and r (refroidissant) are added; thus the evolutions of heat during cooling are Ar_1, Ar_2, and Ar_3, and the corresponding points during heating are Ac_1, Ac_2, and Ac_3. The influence of carbon upon the molecular changes taking place in steel can best be observed by submitting to a microscopical examination samples of steel which have been heated to various temperatures and suddenly cooled by quenching in water or mercury, in order to fix as far as possible the structure which they possess at the temperature at which they are quenched. Let us consider, for example, a steel containing 0·4 per cent. of carbon. If such a steel is quenched at a temperature above Ar_2 its structure will be found to consist entirely of an acicular constituent, of which photograph 1, No. 3, represents a typical example, and which is known as **martensite**. The highest powers of the microscope are unable to resolve this material with the needle-like structure into different components, and it is evidently a solid solution of carbon in iron. It is a hard, brittle substance, and is the chief constituent of hardened steels.

If, now, the same steel is quenched from a temperature between Ar_2 and Ar_1 the same constituent will be observed, but in this case it is not the only constituent, but occurs in patches surrounded by a structureless and much softer material which is practically pure iron and is described as ferrite. Again, the same steel quenched at a temperature below Ar_1, or allowed to cool naturally, will be found to possess a different structure. It still contains two constituents, but the martensite has undergone a change. The carbon is no longer dissolved in the iron, but has separated out as carbide of iron, Fe_3C, and has formed with a part of the free iron a constituent possessing the typical structure of a eutectic as shown in photograph 7. This constituent is known as **pearlite**. It is the eutectic of iron and carbide of iron (or **cementite**), and contains 0·85 per cent of carbon. It is much softer than martensite, and is characteristic of all slowly-cooled steels. Steels containing less than 0·85 per cent. of carbon consist of grains of pearlite embedded in a ground mass of ferrite, and are sometimes described as **hypo-eutectic**, while those containing more than 0·85 per cent. of carbon consist of massive cementite embedded in a ground mass of pearlite and are known as hyper-eutectic. Hyper-eutectic steels quenched at temperatures above Ar_1 consist of massive cementite embedded in martensite; while in hypo-eutectic steels the quantity of martensite varies and is greater with the higher quenching temperature; from which it will be seen that martensite does not possess a definite composition, but is a solution of variable concentration.

The accompanying diagram (fig. 81), which is due to Mr. Sauveur, shows the composition of a number of steels quenched at different temperatures. The effect of carbon upon iron may be summed up in the following manner. Carbon to the extent of 0·85 per cent. is soluble in γ-iron, and lowers the temperature at which the molecular change from γ to β- and α-iron takes place. It is, however, not soluble in α-iron; and when the molecular change does take place it is accompanied by the separation of carbide of iron in the form of a eutectic.

The complete equilibrium diagram of the iron-carbon alloys was plotted by Roozeboom from Roberts-Austen's results, and has been confirmed, with only slight modifications, by Carpenter and Keeling. The curve, which is somewhat complicated, is shown in the accompanying diagram (fig. 82), and in order to make its meaning clear we will follow the changes which occur during the cooling of one or two typical steels. Take first the case of a steel containing 0·2 per cent. of carbon cooling down from a molten condition. The first break in the curve occurs at a point in the line AB when the metal begins to solidify, and a few degrees lower (represented by a point in the line ba) solidification is complete. The mass now consists of a solid solution of carbon in γ-iron (martensite), and no further change occurs until the line GO is reached at about 820° (Ar_3). At this point pure iron in the β-condition separates out, the carbon being concentrated in the remaining martensite. The next point occurs when the line MO is reached at 776° (Ar_2), when the free β-iron changes into α-iron, and becomes magnetic. The last change occurs when the line PSK is reached at 690° (Ar_1), at which temperature the martensite breaks down into pearlite.

Although the point Ar_1 has just been described as the last

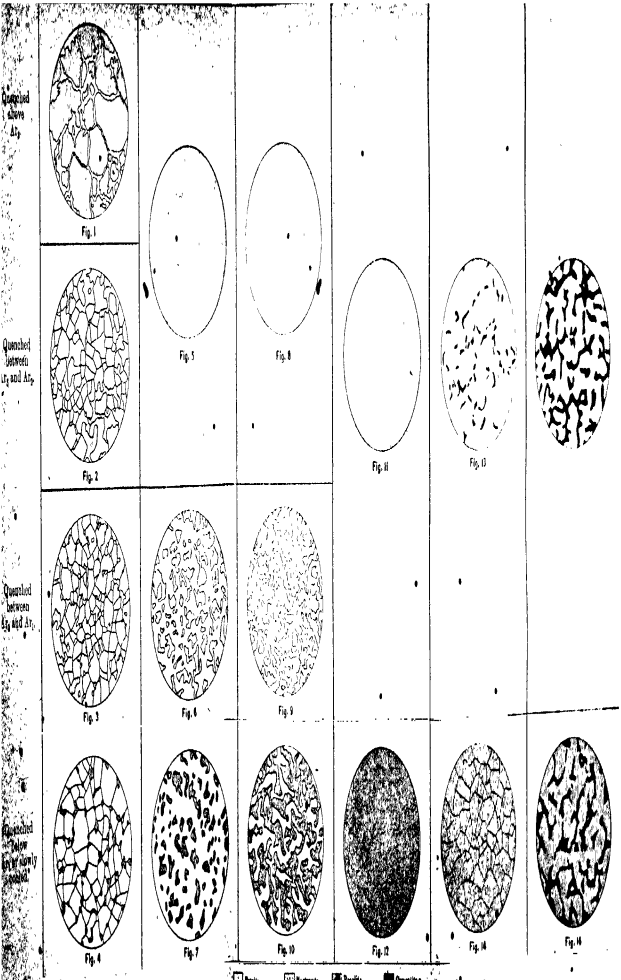

Fig. 81.—Diagrammatic Illustration of Microstructure of Steel, quenched above, between, and below the Critical Points.

change occurring in a cooling steel, the expression is not strictly accurate, as Roberts-Austen detected, and Carpenter and Keeling

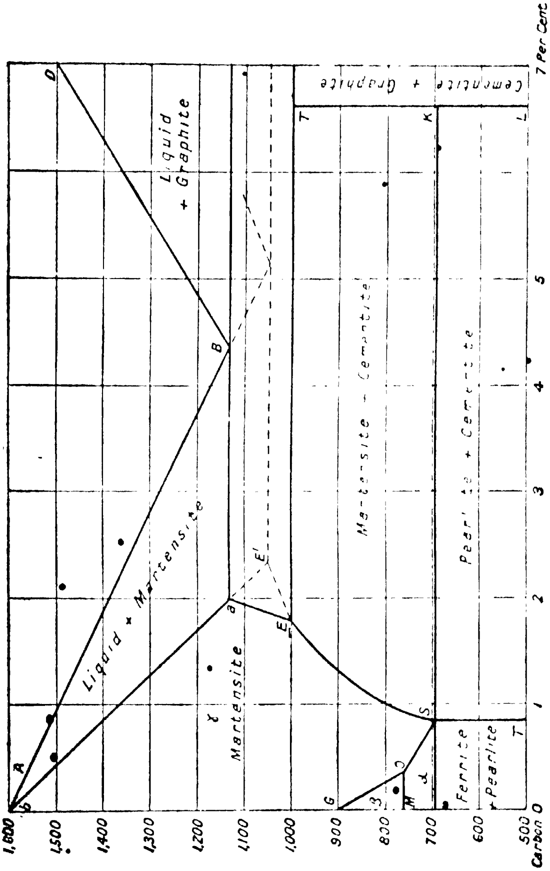

FIG. 82.—Equilibrium Diagram of Iron-carbon Alloys.

have confirmed, the existence of a change, shown by an irregularity in the cooling curves of a wide range of alloys, at 600°. This point has been described as Ar_0, but Rosenhain has shown that it is due to the tube in which the cooling takes place, and is not connected with the steel itself.

The changes occurring in a steel containing 0·5 per cent. of carbon are similar, except that α-iron separates directly from martensite at about 750° without the preliminary separation of β-iron.

The case of a steel containing 1 per cent. of carbon is somewhat different. The solidification of the metal extends over a range of nearly 100°, that is to say, the distance between the points on the lines AB and ba. As before, the solid metal consists of martensite; but when the line SE is reached at a temperature of 850° massive cementite separates out in the martensite. At 690° the martensite breaks down into pearlite, and the result consists of massive cementite embedded in a matrix of pearlite. As a last example, let us consider the case of an alloy containing 3 per cent. of carbon. At 1240° martensite begins to solidify, but as γ-iron is only capable of dissolving about 2 per cent. of carbon to form martensite, it follows that the separation of martensite is accompanied by a concentration of carbon in the mother liquor. This concentration continues until the carbon reaches 4·3 per cent., when the eutectic of martensite and graphite separates. As the temperature falls below 1000° part of the graphite again enters into combination, with the formation of cementite, so that the metal consists of cementite and martensite; and at 690° the martensite breaks down into pearlite, the final result being cementite and pearlite with free carbon or graphite. When more than 4·3 per cent. of carbon is present, graphite is the first constituent to separate out.

The microscopical appearance of the important constituents of steel has already been described; but other constituents, or perhaps it would be more correct to say modifications of these constituents, may be produced by thermal treatment, and they must be briefly described.

Troostite is an intermediate or transitional product which is formed during the transformation of martensite into pearlite, and is found in steels which have been quenched at the critical temperature Ar_1. It is softer than martensite, and owing to the fact that it can only exist within a very limited range of temperature it is seldom met with. Photograph 42, which is by Osmond, shows the appearance of troostite under the microscope.

Sorbite is also an intermediate formation between martensite and pearlite, but is more closely related to pearlite. It has been described as "un-segregated pearlite," or pearlite in which the separation of ferrite and cementite is imperfect owing to rapid cooling. Sorbite is found in small samples which have been cooled in air, and in larger samples which have been quenched in water towards the end of the recalescence, or quenched in molten lead. It is also produced by heating martensite to a blue colour. It is hardly possible to define the intermediate formations between martensite and pearlite, as there appears to be a gradual change with no sharply-defined limits through troostite, troosto-sorbite, sorbite, granular pearlite, and lamellar pearlite.

Austenite is found in steels containing more than 1·2 per cent of carbon which have been quenched from a temperature above 1000° in water cooled to zero, or better, in a freezing mixture. The appearance of austenite is shown in photograph 1, No. 4, the lighter constituent being austenite and the darker martensite. It is softer than martensite, and, owing to the fact that it is only stable at high temperatures, Baron Juptner has suggested that it may be a solution of elementary carbon in iron.

As regards the microscopical methods of detecting the constituents of steel and their distinguishing characteristics, a few words may be useful.

The structure of ordinary steels may be made apparent by etching with nitric acid, but it is difficult with so strong a reagent to regulate the degree of etching. Many years ago Osmond recommended an aqueous extract of liquorice root as an etching reagent used in the following way:—A piece of smooth parchment was moistened with the liquorice extract and a small quantity of precipitated calcium sulphate added. The specimen was then rubbed vigorously upon the moist parchment until the structure was revealed. The calcium sulphate serves the purpose of a polishing powder, and keeps the surface of the steel clean. This is the combined "polish attack," as it is sometimes called. Subsequently Osmond showed that a 2 per cent solution of ammonium nitrate might be used in place of the liquorice extract, and is more convenient on account of its uniformity. By either of these methods the various constituents can be distinguished as follows:—

Pearlite by the unequal etching of its constituents.

Sorbite is coloured yellow to dark brown.

Troostite, yellow, brown or blue bands merging into each other.

Martensite shows its characteristic acicular structure.

Ferrite by its crystalline structure.

Cementite and austenite are unaffected.

In order to distinguish martensite from austenite, Osmond connects the sample with the positive pole of a bichromate battery and immerses it in a 10 per cent. solution of ammonium chloride, the negative pole consisting of platinum or iron foil. In this way the martensite is coloured successively yellow, brown and black.

The combined polishing and etching produces very beautiful specimens, and Osmond's photographs, taken some years ago, have never been surpassed, but the method is somewhat tedious where perfect results are not essential, and an etching reagent, consisting of a 5 per cent. solution of picric acid in alcohol, as suggested by Igewski, is now largely used. With this reagent no rubbing is necessary, the specimen merely being immersed in the solution, washed in alcohol, and dried. One of the great advantages of this method is the fact that although extremely rapid there is little risk of obtaining misleading effects by over-etching, as is so often the case with nitric acid. A great many other more or less complex etching agents have been suggested, which it is unnecessary to mention in detail; but an example may be given of a complex reagent which it is claimed by its author, M. Kourbatoff, will colour troostite and troosto-sorbite, leaving other constituents unaffected. This reagent is composed of one part of ethyl alcohol, one part of methyl alcohol, and one part of a 4 per cent. solution of nitric acid in acetic anhydride.

From what has been said of the constituents of steel and their formation, it will be seen that austenite and troostite are very rarely met with, whereas ferrite and pearlite are found in all the classes of steel used for constructional purposes such as bridge work, railway and tram rails, etc. Cementite is found in all high carbon steels, and martensite is characteristic of all steels hardened by quenching, and, as will be seen later, certain steels which remain hard without quenching Sorbite is sometimes found in steels which have been quenched after rolling.

So far, only pure iron carbon alloys have been dealt with, but commercial steels invariably contain small quantities of other elements; these have an important influence on the quality of the alloys, and must be considered The more important of these elements are silicon, sulphur, phosphorus, and manganese

Silicon forms a solid solution with iron, and appears to go into solution in the form of a silicide FeSi It is therefore not detected under the microscope On the other hand, a certain amount of silicon is frequently found in steel in the form of silicate slag In good steel the quantity of slag is very small, but in inferior steels it is ocasionally found in considerable quantities The ordinary chemical analysis fails to distinguish between silicate and silicide, only the total silicon content being returned, but a microscopical examination reveals the existence of silicates

Sulphur invariably occurs as manganese sulphide in steel It is of a pale slate colour, somewhat lighter than manganese silicate Unlike the silicates, however, it is elongated without being broken during the rolling of the steel, and is found in long threads in rolled steels. Photograph 39 shows both manganese sulphide and iron silicate occurring side by side, and photograph 38 shows a patch of manganese sulphide and manganese silicate occurring together On treating with dilute acid the manganese sulphide is dissolved out, leaving pits, while the silicate remains unattacked.

Phosphorus forms a solid solution with iron, entering into solution as phosphide of iron, Fe_3P Phosphide of iron, especially when present in fairly large quantities, frequently segregates, the parts of the steel rich in phosphide being harder and whiter than the rest of the metal. These segregations are apparent during the turning, cutting, or filing of the steel, and are known by the workmen as "ghosts"

Manganese occurs in steel in at least three forms It combines with all the sulphur present to form manganese sulphide, as already noted. It also occurs, to a certain extent, as manganese silicate, and most probably as manganese silicide. Moreover, it forms with carbide of iron a double carbide which is represented by Carnot and Goutal as $4Fe_3C, Mn_3C$, and by Behrens as $Fe_7Mn_2C_3$. Considering the experimental difficulties involved in the determination of the composition of these carbides, the results agree remarkably well, as is readily seen if the formulæ are brought to the same value in manganese. They then become $Fe_{24}Mn_6C_{10}$, and $Fe_{21}Mn_6C_9$.

In addition to the elements already mentioned several others, such as arsenic, copper, nitrogen, oxygen, and hydrogen, are nearly always found in small quantities in steel. Their influence (in the quantities in which they are usually found in steel) is either less important, as in the case of arsenic and copper, or very imperfectly understood, as in the case of nitrogen and hydrogen, and it is impossible to do more than mention them here.

From the foregoing description of the constituents to be found in an ordinary sample of steel it follows that the microscopical examination should be conducted in three stages. First, the specimen should receive as perfect a polish as possible and be carefully examined in order to determine the quantity and nature of the slag present. Then it should be lightly etched in order to reveal the quantity and condition of the carbide, that is to say, whether it occurs as pearlite, sorbite, etc. Finally, it should be deeply etched to show up its crystalline structure.

Although the series of iron carbon alloys possess a very wide range of properties, it has been found that they may in many cases be improved by the addition of another element. The resulting alloys are largely used at the present time, and constitute the class of alloys frequently referred to as "special steels." The most important of these alloys are the nickel steels, manganese steels, chrome steels, and tungsten steels, while a number of others, including vanadium, molybdenum, silicon, and aluminium, are also used industrially. More recently quaternary alloys containing two of these elements have attracted considerable attention. The principal characteristics of the more important of these alloys will be briefly considered. It may here be pointed out, however, that in all the steels now used for the purposes of construction the result of adding a third component is the production of a stronger and harder alloy than the simple iron carbon steel, but without any corresponding increase in brittleness. That is to say, a triple alloy containing 0·3 per cent. of carbon can be obtained as strong as an ordinary steel containing 0·7 per cent., or more, of carbon, but without the brittleness of the simple iron-carbon steel.

Nickel Steels

Nickel alloys with iron in all proportions and some of the alloys possess remarkable properties. As regards the effect of nickel upon the molecular changes which occur during the cooling of steel, Osmond has shown that in low carbon steels the changes Ar_3, Ar_2, and Ar_1 are successively lowered. With 4 per cent of nickel, Ar_2 and Ar_1 unite at about 640°, and with 8 per cent of nickel only one change takes place at about 510°.

In 1889 Hopkinson showed that a nickel steel containing 25 per cent of nickel was non-magnetic at the ordinary temperature, but when cooled to 0° it became slightly magnetic, and at −50° was strongly magnetic. Moreover on again reaching the ordinary temperature it remained magnetic, and did not lose this property until raised to a temperature of 580°.

Since the communication of these results by Hopkinson the magnetic properties of these alloys have been carefully studied, and the figures obtained by Osmond, showing the temperatures at which magnetism appears during cooling and disappears during heating, are plotted in the form of a curve (fig. 84). It will be seen that the alloys may be divided into two groups, the reversible and the irreversible. Dumas has redetermined the temperatures of transformation with special reference to the alloys lying between the two groups, containing 20 to 30 per cent of nickel, but the results are somewhat irregular.

Another equally interesting property of the nickel-iron alloys is that of expansion or dilatation. Guillaume has determined the variation of dilatation of the series of alloys, and he finds that the addition of nickel causes a decrease in the dilatation until 35 to 36 per cent of nickel is reached, after which there is a rapid increase. In some cases the alloys containing about 36 per cent. of nickel show a slight contraction with rise of temperature. It is thus possible to obtain alloys possessing any desired coefficient of expansion from that of iron or nickel down to zero, and this valuable property of the alloys has been made use of in several industries. Formerly platinum was the only metal with a coefficient of expansion sufficiently near that of glass to enable

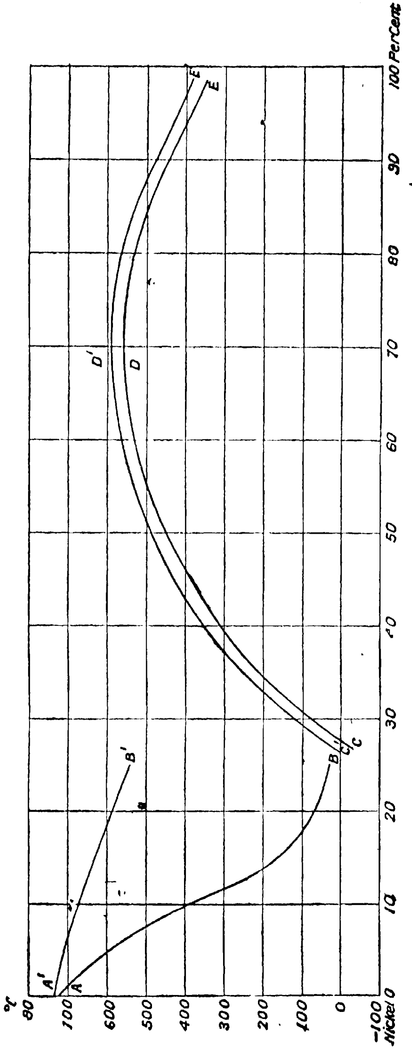

Fig. 83.—Magnetic Transformations of Nickel Steels.

it to be used in the manufacture of incandescent electric lamps without risk of fracture at the base of the lamp where the wire was fused into the glass. Platinum, however, has now been entirely replaced for this purpose by an alloy of nickel and iron containing 46 per cent. of nickel and about 0·15 per cent. of carbon, which Guillaume has named platinite. An alloy possessing no coefficient of expansion with rise of temperature is obviously of the greatest importance in the manufacture of watches, clocks, and scientific instruments, as well as standard measures of length, measuring tapes, etc. For this purpose Guillaume has introduced an alloy containing 36 per cent. of nickel and about 0·2 per cent. of carbon under the name of invar[1]. Every batch of the alloy is tested, and it is sold in three grades — extra superior, superior, and ordinary with guaranteed maximum coefficients of expansion of 0·000008, 0·0000015, and 0·0000025 per one degree respectively. The average figure is, however, well within these limits, and a recent test showed a slight contraction equal to −0·00000005 per one degree. In addition to this valuable property invar is much less readily corroded and oxidised than ordinary steel.

Alloys possessing these remarkable properties might be expected to reveal interesting structures when examined microscopically, and such is found to be the case. The alloys may be divided into three groups according to their structure. Those containing less than 8 per cent. of nickel have the same structure as ordinary carbon steels; those containing from 8 to 25 per cent. possess a martensitic structure characteristic of quenched carbon steels; and those containing more than 25 per cent. exhibit a simple crystalline structure characteristic of pure metals and homogeneous solid solutions. These limits are not absolutely defined, as there is no sudden change between the groups, and the change takes place with somewhat lower percentages of nickel if the quantity of carbon is increased. Thus with an alloy containing 0·8 per cent. of carbon the first change occurs when 5 per cent. of nickel is passed; and the second change takes place when 15 per cent. of nickel is reached. Guillet represents the influence of carbon on the structures of the nickel-iron alloys in the form of the diagram here reproduced (fig. 84). The alloys lying within the

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[1] Patented 1897, No. 11 696.

triangle DEF have a pearlitic structure, those within the triangl
BCF are martensitic, and those above the line AF are crystallin

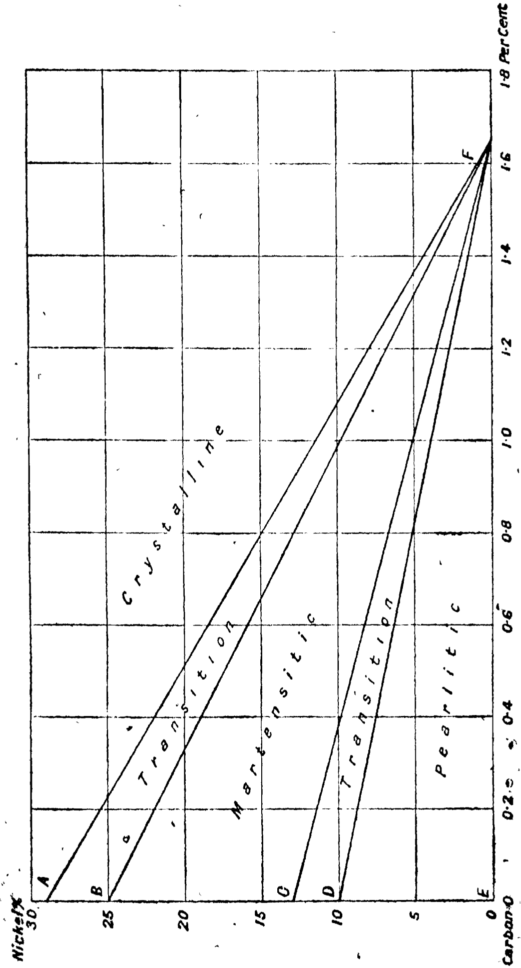

FIG. 84.—Constitution of Nickel Steels.

solid solutions. The triangles ABF and CDF represent transiti stages between the pearlitic and martensitic, and the martensitic and crystalline respectively.

Knowing the structure of the alloys the mechanical properties might be fairly accurately predicted. Determinations of the mechanical properties have been made by a number of workers, including Hadfield and Dundas, whose work must be referred to for detailed figures It is only necessary to say here that with the addition of nickel to steel the tensile strength and elastic limit increases regularly with increasing additions during the pearlitic stage. When the martensitic stage makes its appearance the tensile strength and elastic limit also rapidly, reaching a maximum about the middle of the martensitic stage, and then decrease rapidly until the crystalline stage is reached, when the variations are small and regular. The rapid rise in the tensile strength in the martensitic steels is accompanied by a corresponding fall in the elongation and contraction.

The pearlitic steels are stronger than the corresponding carbon steels, though the increase is not very great. They are very little harder, but their resistance to shock is considerable.

The martensitic steels are very much stronger and harder than ordinary steels of the same carbon content. They show a high elastic limit, and their resistance to shock is moderate.

The crystalline steels possess the usual properties of pure metals and homogeneous solutions with similar structures. They are not particularly hard, and have no great degree of strength. They are, however, extremely ductile, and withstand shock remarkably well.

As regards the influence of heat treatment, it may be mentioned that the pearlitic steels quenched from a temperature above their transformation point are converted into martensitic steels just as in the case of carbon steels. The quenched alloys have, therefore, a higher tensile strength, but are brittle. The martensitic steels containing low percentages of nickel are also hardened by quenching, owing to the fact that the quenched alloys consist entirely of martensite; whereas in the slowly-cooled alloys a certain amount of free α-iron separates out between the martensite. The steels containing higher percentages of nickel are unaffected by quenching, and those bordering on the third or crystalline group of alloys are slightly softened. By cooling in liquid air some of the crystalline steels can be transformed into those with martensitic structures.

Considering the structure of the alloys together with the information obtained from their cooling curves, it will be seen that nickel lowers the points of transformation of steel. When more than 8 per cent. of nickel is present the change Ar_1 does not take place until the alloy is cooled below the normal atmospheric temperature, with the result that these steels possess the martensitic structure and mechanical properties characteristic of steels hardened by quenching. Nickel steels, therefore, containing from 8 to 25 per cent. of nickel may be classed as self-hardening steels.

Nickel steel possesses a high electrical resistance, and an alloy containing 25 per cent. of nickel and about 0·8 per cent. of carbon, possessing a resistance about ten times that of iron, is used in the manufacture of resistance coils.

The following table gives the composition of a number of nickel-iron alloys and the purposes for which they are employed.

IRON-NICKEL ALLOYS.

Composition.		Applications.
C.	Ni.	
0·05 to 0·15	2 to 3	Weldless steel tubes.
0·2 to 0·4	2 to 3	Gun steel.
0·3 to 0·5	1 to 3	Cranks, crank shafts, etc.
0·2	3 to 3·5	Boiler plates.
0·5	3·5	Tyre steel.
0·2 to 0·4	5 to 6	Connecting rods, axles, etc.
0·25	30 to 32	Motor valves.
0·7 to 0·9	25	Ferro-nickel resistance wire.
0·2	36	Invar (Guillaume's non-expansible alloy).
0·15	46	Guillaume's platinite.

Manganese Steels.

Manganese, like nickel, lowers the temperatures at which the molecular changes take place in steel. Osmond has shown that when 3 per cent. of manganese is reached the alloy possesses only one critical temperature, Ar_{321}, at about 400°; and with 7 per cent. of manganese this change does not take place above the ordinary temperature. The microstructure of the alloys is also similar to those of nickel. In the case of low carbon steels those containing less than 5 per cent. of manganese have a pearlitic structure; those containing from 5 to 12 per cent. are martensitic, and beyond 12 per cent. the structure is crystalline. With a higher percentage of carbon smaller quantities of manganese suffice to produce the same structure; thus with 0·8 per cent. of carbon a change in structure occurs when more than 3 per cent. of manganese is reached, but in the high-carbon alloys Guillet is of opinion that the constituent is troostite and not martensite It is also worthy of note that in the pearlitic steels the pearlite, which contains a double carbide of iron and manganese, is much more broken up and granular than that found in ordinary carbon steels, and has some resemblance to sorbite.

The influence of heat treatment upon manganese steels is very much the same as in the case of the nickel steels

A similar diagram to that employed in the case of the nickel alloys may be used to indicate the structure of the manganese alloys (fig. 85). The increase in tensile strength and elastic limit due to the introduction of manganese into steel is small during the pearlitic stage, but rises when the martensitic stage is reached. These steels are extremely hard and brittle, and are of no practical use. When the crystalline stage is reached, however, the alloys lose their brittle character, but retain a very considerable degree of strength and hardness These steels are represented by the well-known Hadfield manganese steel, which contains about 13 per cent. of manganese and 1 per cent. of carbon.

Chromium Steels.

The influence of chromium on steel is somewhat different to that of nickel and manganese. It appears to raise slightly the point Ar_1; but according to Osmond the point of magnetic transformation is only slightly affected.

As regards the constitution of the chromium steels, those containing less than 7 per cent. of chromium are pearlitic, and those containing from 7 to about 15 per cent. are martensitic. With more than 15 per cent. a double carbide makes its appearance in the form of small particles, which are perfectly white and very hard. As in the case of nickel and manganese steels these changes

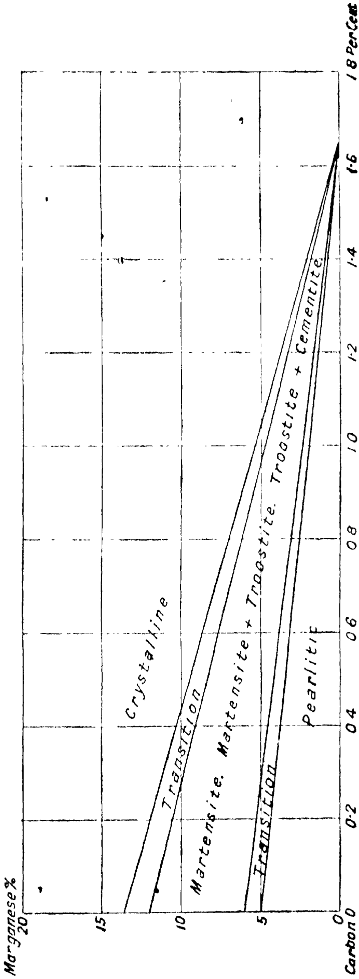

FIG. 85.—Constitution of Manganese Steels.

occur with smaller percentages of the metal when the carbon content is higher and the martensite tends to alter into troostite. In the alloy containing 0·8 per cent. of carbon the structure ceases to be pearlitic with 3 per cent. of chromium. The pearlitic steels are stronger and harder than the corresponding carbon steels, but somewhat more brittle. Those possessing a martensitic structure are extremely hard and give high tensile tests, but are not as brittle as might be expected until the chromium present is sufficient to produce the double carbide. When an appreciable quantity of this constituent is present the alloys give low tensile tests and good elongations, as in the case of the crystalline alloys of nickel and manganese, but, unlike these alloys, they are very brittle on account of the presence of the double carbide

As regards heat treatment, the pearlitic steels are converted into the hard martensitic variety by quenching, and the martensitic and carbide steels are slightly softened by the same treatment. Only the pearlitic steels are of any industrial value They are largely used as tool-steels, and also for armour plates and armour-piercing projectiles. The steel used in the manufacture of projectiles contains about 1 per cent. of carbon and 2 to 3 per cent. of chromium. Chromium is also occasionally added to steel intended for springs and tyres, and is frequently a constituent of high-class file-steels.

Tungsten Steels.

The constitution of the tungsten steels is less complex than those previously considered With less than 10 per cent. of tungsten the alloys of low carbon content are pearlitic, but when more than this quantity is present a double carbide of iron and tungsten makes its appearance. In the high carbon steels this double carbide appears when 5 per cent. of tungsten is present; but in neither case does an intermediate martensitic structure occur, as in the chromium steels. The addition of tungsten increases the hardness and tensile strength of steel and, to a less extent, the elastic limit, without, however, any noticeable increase in brittleness. With the formation of the double carbide the alloy becomes very brittle and hard, with a high tensile strength and low elastic limit and elongation. It is therefore the pearlitic steels approaching the double carbide alloys that are of industrial value.

The effect of quenching on these alloys is similar to that produced in carbon steels, but much more marked; and by simply cooling in air they attain sufficient hardness to enable them to be used as tool-steels. These steels are represented by the well-known Mushet self-hardening steels. The composition of a number of Mushet steels is shown in the table:—

Steel.	C.	Si.	Mn.	W.
Mushet steel	1·99	0·09	0·19	7·81
,, ,, ...	2·30	1·05	2·57	6·12
,, ,, ...	2·00	1·60	1·72	8·22
Crescent ,, ...	2·06	0·05	2·66	6·79
Imperial ,, ...	1·60	0·16	2·11	6·38

Tungsten steels are occasionally used in the manufacture of springs, the alloys employed for this purpose containing about 0·5 per cent. of carbon and 0·6 per cent. of tungsten; they are also used in the manufacture of permanent magnets, the steel in this case containing either 0·6 to 0·7 per cent. of carbon and 4 to 6 per cent. of tungsten, or 1·0 to 1·2 per cent. of carbon and 7 to 8 per cent. of tungsten.

Molybdenum Steels.

The effect of molybdenum on steel is very similar to that of tungsten, but much more strongly marked. That is to say, a smaller percentage of molybdenum is necessary to produce the same result. Thus in carbon steels containing 0·8 per cent. of carbon the double carbide of iron and molybdenum is formed when more than 1 per cent. of molybdenum is present. One part of molybdenum, therefore, is equivalent to about 4·5 parts of tungsten.

The pearlitic steels have a high tensile strength and elastic limit, which increases with the percentage of molybdenum; while the elongation and brittleness show a slight falling-off.

Molybdenum steels have been used as tool-steels, but usually in conjunction with tungsten, and sometimes with chromium and tungsten. The principal use of molybdenum steel, however, is for the manufacture of permanent magnets, for which purpose they are superior to tungsten steels. The usual composition of these steels is about 1·0 to 1·5 per cent. of carbon and 3 to 4 per cent. of molybdenum.

Silicon Steels.

The constitution of the silicon steels differs from those previously considered, inasmuch as silicon forms neither a double carbide nor a solid solution in all proportions with iron. It combines with iron to form a silicide corresponding to the formula FeSi, which, within certain limits, forms a solid solution with iron. It follows that the constitution of the silicon steels is independent of the carbon present. With less than 5 per cent. of silicon the alloys possess the same structure as ordinary steels; but beyond 5 per cent. the iron containing silicide in solution appears to be incapable of dissolving the same quantity of carbon, and a part of the carbon is thrown out in the graphitic condition. When the silicon exceeds 7 per cent. the whole of the carbon is found as graphite.

Silicon steels are harder than ordinary carbon steels, and possess a higher tensile strength and elastic limit; but their resistance to shock is not great when more than 2 per cent. of silicon is present. Those containing free graphite are useless.

Quenching hardens the pearlitic steels, and the effect is much greater than in the case of carbon steels.

The principal application of silicon steel is in the manufacture of springs, the percentage of silicon for this purpose varying from 0·8 to 2·0, with carbon from 0 7 to 0·4 respectively. In addition to these true silicon steels there are steels containing somewhat higher percentages of silicon than ordinarily met with in carbon steels. In the manufacture of these steels silicon in the form of ferrosilicon is added to the metal in the ladle before teeming, and answers the double purpose of eliminating oxygen and adding silicon. The destruction of oxide gives a fluid metal which yields castings free from slag and blowholes; while the excess of silicon renders the steels stronger, harder, and tougher. Steels of this description, such as the well-known Sandberg silicon rail-steel, give an increased life of more than 100 per cent. in actual use.

Alloys containing high percentages of silicon are now largely used in the cast state under the name of tantiron for many purposes where a metal possessing a great resistance to corrosion is required. The alloy is brittle and requires considerable skill in casting owing to its shrinkage, but in the form of evaporating pans, basins, etc., has been of great service in chemical industries. An analysis of a sample of the alloy gave the following results:—

Iron	82·50
Silicon	13·99
Carbon	1·12
Manganese	0·80
Phosphorus	0·53
Sulphur	0·10

Vanadium Steels

Vanadium appears to exert a stronger influence on the properties of steel than any other metal. With less than 0 7 per cent. of vanadium the alloys are pearlitic, but with more than this amount a double carbide is formed

The tensile strength, elastic limit, and hardness rise rapidly with the addition of vanadium, while the elongation only decreases slightly, and there is no increase in brittleness. With the appearance of the double carbide, however, the brittleness rapidly increases, although the elongation and reduction of area increase and the tensile strength and elastic limit decrease.

The pearlitic steels are hardened by quenching in the same way as carbon steels, but to a greater degree.

Only those steels containing less than 0·7 per cent. of vanadium —that is to say, those consisting of pearlite—are of any industrial value, and the addition of vanadium up to this amount possesses the unique property of greatly increasing the tensile strength and elastic limit of the steel without any corresponding decrease in the elongation or increase in brittleness. Unfortunately, the high price of vanadium is a serious drawback to its use except for special steels.

Quaternary Steels.

In addition to the ternary steels just described a large number of quaternary, or even more complex, steels are in use at the present time. It is impossible to describe these complex steels, but it may be remarked that their constitution is in every way comparable with the ternary alloys, and not more complicated. By adding two or more metals, however, it is often possible to obtain a steel combining the useful properties conferred by each of the added metals singly.

The more important of the quaternary steels are the nickel-chromium, chromium-tungsten, and manganese-silicon, while the nickel-vanadium, chrome-vanadium, and nickel-tungsten have been described and appear to possess properties which should ensure

for them a successful future. Among the more complex steels may be mentioned the chrome-tungsten-molybdenum steels, which, in the form of tools, may be used at a speed which maintains them at a red heat without suffering any serious deterioration.

As regards the applications of the quaternary steels mentioned above, the nickel-chrome steels are used for armour plates and armour-piercing projectiles as well as for the shafts and gearing of motors. The composition of the steels employed for these purposes is as follows.—

	C	Ni	Cr
Armour plates . . .	0·2 to 0·5	3·0 to 5·0	1·0 to 2·0
Projectiles	0·5 to 0·6	2	2
Shafts, gearing, etc. . .	0·2 to 0·5	2·5	0·25 to 0·5

Chrome-tungsten steels are used entirely as high speed tool-steel. The following table shows the composition of a number of steels used for high speed work. In these steels manganese is always low, and silicon usually about 0·2 per cent. Carbon varies from 0·2 to 0·8 per cent.

COMPOSITION OF CHROME-TUNGSTEN TOOL STEELS.

Number	C	W	Cr	Mo.
1	0·71	12·0	3·0	...
2	0·33	15·5	4·5	...
3	0·45	13·0	1·6	
4	0·45	9·5	2·1	...
5	0·60	13·5	8·0	...
6	0·20	7·0	2·1	
7	0·60	9·9	2·8	
8	0·80	18·3	2·9	
9	0·72	13·5	5·2	...
10	0·50	12·0	3·0	1·0
11	0·50	5·0	3·0	4·0

The structural constituents of quaternary steels are the same as those found in ternary steels, and the same relations between structure and mechanical properties hold good. With small additions of other metals the alloys are pearlitic, while with larger additions the structure may consist of martensite, pearlite and carbide, pearlite and graphite, or sorbite and carbide, and with still larger additions, martensite and carbide, martensite and graphite, ferrite and graphite, γ-iron, γ-iron and carbide, or γ-iron and graphite.

The presence of graphite indicates silicon in fairly high percentages.

Martensite indicates nickel, manganese, or chromium; γ-iron ndicates a high percentage of nickel or manganese, or both ogether.

In conclusion, we cannot do better than quote the words of uillet in summing up the alloys of industrial value. After ointing out that the steels containing graphite are useless and hose containing martensite are too hard to be machined, he adds:—"The steels containing carbide are devoid of interest if they also contain γ-iron. It is only when they are pearlitic or sorbitic that they can be of commercial utility, and even in this case they can offer but few special outlets for employment, the most interesting of which are for tool-steels and for ball-bearings. There remain, therefore, but two structures—pearlitic steels, and steels containing γ-iron. The latter can only be obtained by the use of high percentages of nickel, or of manganese, or both, in order to avoid the production of steels easily transformed by quenching, annealing, cooling, etc. These percentages should be higher than is usually believed to be necessary, and the cost of production is proportionately increased. Further, it is necessary to remember that their elastic limits are lower and that they are difficult to machine. This renders their applications exceedingly limited.

"Thus, the following conclusion is arrived at:—Putting aside steels containing pearlite and carbide, or sorbite and carbide, which are of great interest as tool-steels, and in certain special instances for mechanical constructions, and steels containing γ-iron, of which use can only be made in exceptional circumstances, the only structure which should be sought for general purposes is pearlite. This being so, the statement may be further made that steels possessing this structure and its accompanying mechanical properties should not, as a rule, contain high percentages of carbon."

Cast Iron.

Cast iron, or pig-iron, as it comes from the blast furnace is classed or graded according to its fracture. In other words, it is classed according to the condition of the carbon, as the nature of the fracture depends upon whether the carbon exists as graphite or combined carbon. The method of grading and the number of grades vary in different localities, but the iron with the most open grain and grey fracture in which the carbon occurs almost entirely as graphite, is always known as No. 1; and "white" iron, in which the carbon is entirely in the combined form, is the last of the series. The following analyses, due to Ridsdale, show the composition of a series of Cleveland pig-irons:—

	No. 1.	No. 2.	No. 3.	Forge.	Mottled.	White.
Carbon, graphitic	3·20	3·16	3·16	2·72	1·84	...
" combined	trace	0·20	0·48	0·58	1·25	3·05
Silicon	3·50	2·90	2·59	1·93	1·01	0·67
Sulphur	0·05	0·06	0·08	0·10	0·32	0·40
Phosphorus	1·67	1·69	1·57	1·55	1·57	1·60
Manganese	0·68	0·62	0·60	0·75	0·62	0·42

From these figures it will be seen that carbon and silicon are the important elements, and, to a less degree, phosphorus. Moreover, it will be observed that there is a relation between the amount of silicon and the condition of the carbon; as the silicon decreases, more and more of the carbon is found in the combined condition. The constitution of cast iron is, in fact, similar to that of steel in many respects, and we have already seen that silicon combines with iron to form a silicide corresponding to the formula Fe_2Si, which is more soluble in iron than carbon, and throws the carbon out of solution in the form of graphite. The condition of the carbon in cast iron depends, to a certain extent, on the rate of cooling; rapid cooling tending to produce a hard white iron and slow cooling a soft grey iron. It is true that a very soft iron cannot be converted into a white iron or a white iron into a grey by cooling slowly or rapidly; but with the stronger "forge" irons lying between the grey and white, the rate of cooling is a matter of importance. With such an iron a small casting which has cooled rapidly might be found to consist wholly or partly of white iron; while a large casting of the same metal would consist of grey iron. Now, white iron is too hard to be machined; so that the small casting, if it requires any finishing, is unsatisfactory, and a greyer or softer iron must be used. Hence it follows that the percentage of silicon in a cast iron should be regulated according to the size of the casting; the smaller the casting the higher the percentage of silicon.

Sulphur occurs in cast iron as manganese sulphide, where there is sufficient of this metal; but in some white iron, where the sulphur is high, it is found in the form of sulphide of iron surrounding the sulphide of manganese.

Phosphorus combines with iron to form a phosphide Fe_3P, which is soluble in iron to the extent of 1·7 per cent. Beyond this quantity free phosphide separates out and forms a eutectic which melts at about 910°. Phosphorus, however, forms another eutectic with the carbide, which Stead has described as the phospho-carbide eutectic. This eutectic has a much finer structure than the iron and phosphide eutectic, and frequently forms fringes, as shown in photograph 7 Owing to the low melting-point of the phosphide, eutectic iron high in phosphorus is extremely fluid and gives fine castings, but the metal is brittle. The constituents of grey cast iron, therefore, are graphite, ferrite containing phosphide and silicide in solution, phosphide of iron, sulphide of manganese, and carbide in the form of a phospho-carbide eutectic. In white iron the constituents are manganese sulphide, iron sulphide, carbide, and phosphide.

Stead has shown that where massive carbide and phosphide occur together, the only satisfactory way of distinguishing between them is by heat-tinting the specimen, when the carbide will be found to oxidise more readily than the phosphide.

As regards the composition of cast iron for various purposes, sulphur should never exceed 0·09 per cent. and phosphorus should not exceed 0·7 per cent. if strength is required. Manganese should not exceed 0·7 per cent. except for chilled castings. Silicon varies according to whether a hard, medium, or soft iron is required, but average figures may be taken as 1·4 per cent. for hard iron, 1·8 per cent. for medium iron, and 2·5 per cent. for soft iron. These figures are, however, only approximate, and allowance must be made for the size of the casting.

Alloys Employed in the Manufacture of Steel.

Within the last few years there has been a great demand for alloys of iron to be used in steel manufacture, both as deoxidisers and as a means of introducing a new constituent. These alloys are made either in the blast furnace or the electric furnace, and sometimes by means of Goldschmidt's aluminium reduction process. The alloys produced in the electric furnace are purer and contain higher percentages of the metals (other than iron) than those made in the blast furnace. The first of the "ferro" alloys to be used in steel manufacture was ferro-manganese, which was introduced in the early days of the Bessemer process, as it was found to greatly improve the quality of the steel.

Ferro-manganese is made in the blast furnace. It consists essentially of iron and manganese, the latter varying from 40 to nearly 90 per cent., and about 6 per cent. of carbon. The following analyses show the composition of a number of samples of commercial ferro-manganese :—

	1.	2.	3.	4.	5.	6.	7.
Manganese . . .	87·92	84·33	80·62	70·55	61·81	50·60	41·45
Carbon . . .	6·31	6·95	7·00	6·68	6·28	6·12	5·62
Silicon . . .	0·53	0·54	0·30	0·49	0·63	0·14	0·10
Phosphorus . . .	0·15	0·15	0·16	0·20	0·16	0·11	0·09

Manganese behaves partly as a deoxidiser. Its existence in steel in the form of sulphide, silicate, and carbide has already been discussed.

Spiegeleisen is a ferro-manganese containing a lower percentage of manganese than ordinary ferro-manganese. It varies from about 10 to 30 per cent. of manganese

Silicon spiegel is an alloy of iron and manganese, in which these metals occur as silicides. The alloy is made both in the blast furnace and the electric furnace, some of those made in the electric furnace being practically pure silicide of manganese. The silicon in these alloys is a powerful deoxidising agent. The following analyses show the composition of several commercial silico-spiegels produced in the blast furnace and in the electric furnace :—

SILICON SPIEGEL MADE IN BLAST FURNACE.

	1.	2.	3.	4.	5.	6.
Manganese	20·87	20·39	17·50	18·90	20·32	20·50
Silicon	14·23	13·31	12·52	11·80	10·33	9·45
Carbon	1·39	1·51	1·05	1·89	1·26	1·45
Phosphorus	0·10	0·01	0·06	0·08	0·07	0·07

SILICON SPIEGEL MADE IN ELECTRIC FURNACE.

	1.	2.	3.	4.	5.
Manganese	74·20	73·50	55·00	51·00	38·00
Silicon	24·70	24·25	25·00	21·00	21·00
Carbon	0·30	0·65	...	...	...
Phosphorus	0·02	0·05	...	...	...

Ferro-silicon is used both as a deoxidiser and for introducing silicon into steel. It is made both in the blast furnace and the electric furnace.

FERRO-SILICON MADE IN BLAST FURNACE.

	1.	2.	3.	4.	5.	6.	7.
Silicon	17·00	13·45	12·42	11·50	10·37	9·25	8·10
Manganese	1·50	1·71	1·17	1·35	1·86	1·86	2·20
Carbon	0·90	1·21	1·40	1·50	1·51	1·55	1·75
Phosphorus	0·07	0·06	0·05	0·06	0·06	0·05	0·05

FERRO-SILICON MADE IN THE ELECTRIC FURNACE.

	1.	2.	3.	4.
Silicon	32·70	48·70	75·80	94·80
Manganese . . .	0·31	0·13	0·11	0·08
Carbon	0·27	0·09	0·00	0·00
Phosphorus . . .	0·05	0·04	0·02	0·01
Aluminium . . .	0·13	0·17	0·08	0·10

Ferro-chrome is the form in which chromium is introduced into steel. It also is made both in the blast furnace and the electric furnace. The blast furnace alloys contain from about 12 to 40 per cent. of chromium, 1·5 to 2·5 per cent. of manganese, and 5 to 7 per cent. of carbon; while those made in the electric furnace contain about 6·5 per cent. of chromium and 5 to 10 per cent. of carbon. Refined alloys are also made containing as much as 70 per cent. of chromium and only 0·5 to 1·5 per cent. of carbon.

Ferro-tungsten is employed in the manufacture of tungsten-steels. It is made by melting together Swedish iron, charcoal, and tungsten powder, obtained by heating tungstic oxide with charcoal. Three grades of ferro-tungsten are manufactured commercially, the first containing about 65 per cent. of tungsten and 1·5 per cent. of carbon, being intended for open hearth steel; while the second, containing 80 per cent. of tungsten and 1·5 per cent. of carbon, and the third, containing nearly 90 per cent. of tungsten and only about 0·4 per cent. of carbon, are intended for the manufacture of high-class crucible steels.

Ferro-molybdenum, used in the manufacture of molybdenum steels, is made in the same way as ferro-tungsten, which it resembles. It is supplied in various grades containing from 50 to 85 per cent. of molybdenum and 0·4 to 2 or more per cent. of carbon.

Ferro-vanadium is now a commercial alloy, and is made by reducing vanadic acid in presence of iron and charcoal in an electric furnace. The alloy contains from 40 to 50 per cent. of vanadium and about 1 per cent. of carbon.

Ferro-titanium has been suggested as a deoxidiser, and its efficiency for the purpose appears to be undoubted. At present, it is used more particularly as a deoxidiser for cast iron; but it may also be used for steel, and it has recently been suggested as an agent for removing nitrogen from iron and steel. Our knowledge of the part played by nitrogen in iron and steel is very limited, but there is little doubt that it exerts a prejudicial influence on the quality of the metal. An alloy which will remove both oxygen and nitrogen at the same time should have a future before it. Commercial ferro-titanium contains about 50 per cent. of titanium and 3 per cent. of carbon; but a special quality is also supplied containing only 0·5 per cent. of carbon.

Besides these alloys a number of others are used either as deoxidisers, or for introducing another metal, or for both purposes. Among these may be mentioned **ferro-uranium** and **ferro-boron**, used in the manufacture of uranium and boron steels. Such steels are, however, extremely rare. **Ferro-phosphorus**, containing 15 to 20 per cent. of phosphorus, is used as an addition to cast iron, where fluidity is of more importance than strength. Among the complex deoxidisers we have **ferro-aluminium silicide**, containing 45 per cent. silicon and 10 per cent. of aluminium; **ferro-calcium silicide**, containing 70 per cent. of silicon and 15 per cent. of calcium; and **ferro-sodium**, containing 25 per cent. of sodium. Lastly, for the manufacture of quaternary steels we have such alloys as **nickel-chrome**, **nickel-tungsten**, **chrome molybdenum**, and **nickel-molybdenum**.

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CHAPTER XVI.

MISCELLANEOUS ALLOYS.

Amalgams.

THE word *amalgam* is used to describe the alloys of mercury with other metals. Owing to their low melting-points they were the first alloys to be investigated, but recently they have attracted little attention.

Mercury alloys with a number of metals, the union being in many cases accompanied by the evolution of considerable heat, but very few of the amalgams have been put to any use, and the applications of those that are used industrially are strictly limited.

The principal amalgams are those of tin, copper, cadmium, bismuth, sodium, silver, gold, and palladium.

Tin-amalgams are made by adding mercury to molten tin. The amalgam of equal parts of mercury and tin is a brittle solid; but with more mercury a plastic mass is obtained which becomes hard in the course of a few days. This and similar alloys containing cadmium, silver, or gold, are used by dentists for stopping teeth. The amalgams are used in a plastic condition, and harden with little or no expansion.

Copper-amalgams.—Copper does not alloy readily with mercury under ordinary conditions. By mixing mercury with precipitated copper in presence of mercuric nitrate solution, however, the mercury unites with the copper to form an amalgam.

Copper-amalgam is plastic when newly made, but becomes hard in a day or two. It may be softened again by immersing it in boiling water or by simply pounding it; and it is capable of being hammered, rolled, and polished. It hardens without expanding or contracting, and on this account makes an excellent stopping for teeth, while at the same time it has the property of rendering the tooth in contact with it extremely hard. Unfortunately, however, it is rapidly blackened by sulphur compounds, and it is now seldom used. Copper-amalgam can be used as a cement for metals, and is also used for cementing china and porcelain.

Cadmium and **palladium-amalgams** are both employed as dental amalgams, the latter being considered the best amalgam for the purpose.

Bismuth-amalgam, either in the pure state or with additions of lead and tin, is occasionally used for silvering glass.

Silver- and **gold-amalgams** are of some interest on account of their formation in the extraction of gold and silver from their ores. Silver-amalgam is also used for silvering glass. Silver and mercury form a definite compound, corresponding to the formula Ag_2Hg_2. By squeezing the excess of mercury through chamois leather an amalgam of fairly uniform composition is obtained. It contains 43·7 parts of silver to 100 of mercury, or $Ag_2Hg_2 + 4·6$ per cent. mercury.

Gold forms with mercury a compound $AuHg_4$, and the amalgam remaining after squeezing the excess of mercury through chamois leather contains 33 per cent. of gold.

Fusible Metals.

The expression "fusible metal" is usually applied to alloys whose melting-point is below that of tin; and the alloys possessing this property may be either binary, ternary, or quaternary alloys of the metals lead, tin, bismuth, and cadmium. The constitution of the alloys will be sufficiently clear from a consideration of Charpy's work on the ternary alloys of lead, tin, and bismuth. All the metals of the fusible metal group form simple alloys with one another, *i.e.* they form neither compounds nor solid solutions, but consist of practically pure metals and eutectics. Now, we know that a eutectic has a lower melting-point than either of the metals of which it is composed, and that a triple or ternary eutectic has a lower melting-point than a binary eutectic; so that, by combining three metals of low melting-point in the proportions necessary to form the eutectic, we may obtain an alloy whose melting-point is much lower than that of any of the single metals. Similarly, by adding a fourth metal a quaternary eutectic of still lower melting-point may be obtained. Heine has collected formulæ, from all available sources, relating to fusible alloys, and those in the following table are taken from his list.

FUSIBLE ALLOYS.

Composition.				Melting-point.
Lead.	Tin.	Bismuth.	Cadmium.	
25·0	12·5	50·0	12·5	65·5°
26·7	13·3	50·0	10·0	60 – 68
26·0	14·8	52·2	7·0	68·5
28·6	14·3	50·0	7·1	70·0
27·6	10·3	27·6	34·5	75·0
35·1	20·0	35·3	9·5	80·0

The eutectic alloy of lead, tin, and bismuth possesses the property of expanding on cooling, and it is, therefore, used for taking impressions, as the finest details are faithfully reproduced.

The melting-points of fusible alloys may be still further lowered by the addition of mercury.

RARE METAL ALLOYS.

Platinum.—The high price of platinum is a serious drawback to its use in the form of alloys, but a few of these are manufactured industrially. The alloys of platinum and silver have already been referred to as dental alloys, and an alloy of 66 per cent. silver and 34 per cent. platinum is prepared by Messrs Johnson & Matthey as a standard of electrical resistance. A number of alloys of platinum and copper have been suggested from time to time. Cooper's gold, containing 19 per cent. of platinum and 81 per cent. of copper, is said to be malleable, ductile and non-corrodible; it resembles 18-carat gold in appearance.

Platinum containing 10 per cent. of iridium is, perhaps, the most important alloy of platinum. It is now largely used as one of the wires in thermo-couples intended for the measurement of high temperatures, the other wire being of pure platinum. The standard metre made for the Parisian Commission of the International Metrical System in 1870 by Messrs Johnson & Matthey consists of platinum containing 10 per cent. of iridium, and was adopted as the material for the manufacture of the standard weights and measures after a thorough trial lasting over two years.

Platinum containing 10 per cent. of rhodium is also used in thermo-couples for high-temperature measurements.

Among the rare metal alloys may be mentioned the pyrophoric or spark-emitting alloy of cerium with iron and aluminium. These are largely used in automatic cigar lighters.

ALLOYS USED FOR ELECTRICAL RESISTANCES.

The alloys employed in the manufacture of electrical resistances constitute an important class, and although their composition is very variable, it will be convenient to consider them together in the light of the property which renders them of value, rather than separately under the metals of which they are composed. The following table gives the resistance in microhms per cubic centimetre of iron and nickel together with a number of high resistance alloys used in the electrical industry:—

Name.	Description.	Resistance Microhms per c.c.
Iron	...	11·0
Nickel . . .		12·3
German silver .	Containing 7 per cent. nickel	18·0
,, ,, . .	,, 10 ,, ,,	21·0
,, ,, . .	,, 20 ,, ,,	29·0
,, ,, . .	,, 30 ,, ,,	40·2
Platinoid . . .		41·0
Tarnac . . .	Cupro-manganese	41·0
Manganin . . .	Copper-nickel-manganese	42 to 48
Nickelin . . .	Copper-nickel	43·0
Ferry	,, ,,	47·2
Constantan . . .	,, ,, (40 per cent. nickel) .	50·2
Eureka . . .	,, ,, (similar to Constantan)	50·2
Resistin . . .	Copper-manganese	50·2
Ferrozoid . . .	Nickel steel	84·0
Kruppin . . .	,, ,, (28 per cent. nickel)	85·0
Vestalin . . .	,, ,, (similar to Kruppin)	85·1
Nickel chrome . .	Nickel-chromium	93·5
Concordin . . .	...	96·0

The figures given in this table for manganin, nickelin, and resistin, must not be regarded as accurate for all samples known under these names, the composition of the alloys being somewhat variable, as shown by the following analyses collected from various sources:—

Alloy.	Copper.	Nickel	Manganese	Zinc	Iron.
Manganin	84·0	4·0	12·0		...
,,	82·1	2·3	15·0		0·6
,,	58·0	41·0	1·0		.
Nickelin	68·0	32·0			...
,,	55·3	31·1	...	13·1	..
Resistin	86·5		11·7		1·8
,,	84·3		13·4		2·0

The electrical conductivity of alloys has already been referred to, and it will be remembered that Matthiessen divided the metals into three groups:—(1) Those whose conductivity could be represented by a straight line uniting the two pure metals when alloyed together, (2) those in which the addition of either metal to the other causes a rapid decrease in the conductivity, thus giving rise to a U shaped curve; and (3) those in which the decrease in the conductivity of one of the metals is much greater than in the other, thus giving rise to an L shaped curve. Now, on looking at the examples given by Matthiessen in the light of our present knowledge of the constitution of alloys, it will be seen that the metals in Matthiessen's first group are the same as those which with regard to their freezing-point curves Le Chatelier has placed in the first group of his scheme—that is to say, they form a simple series of alloys with a eutectic. Further, the metals of Matthiessen's second group correspond very closely to Le Chatelier's third group—that is to say, the isomorphous or solid solution group. And those in Matthiessen's third group correspond to Le Chatelier's second group. We have, therefore, a definite relation between the constitution of alloys and their electrical conductivity. In alloys consisting of pure metals and a eutectic the conductivity passes gradually from that of the one metal to that of the other; in alloys consisting of solid solutions the conductivity decreases rapidly, and rises again rapidly on the other side; while in those alloys forming solid solutions and compounds, such as the copper-tin and copper-zinc alloys, the conductivity decreases rapidly until the point of saturation is reached and then takes a sudden bend and forms an L-shaped curve. Solid solutions therefore possess a maximum electrical resistance, and all the alloys in the table on p. 322 consist of single homogeneous solid solutions. It is fortunate for the electrical industry that the constitution which confers upon these alloys their high electrical resistance is also the constitution which enables them to be drawn into wire.

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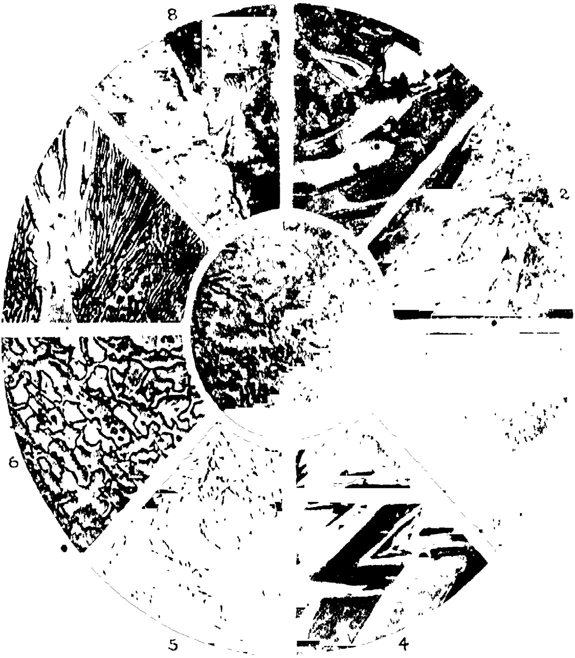
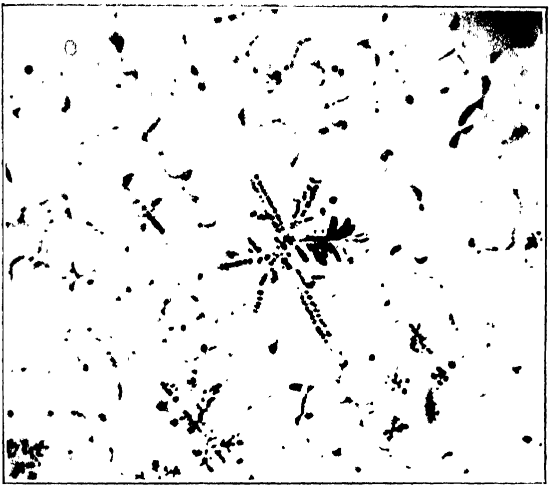


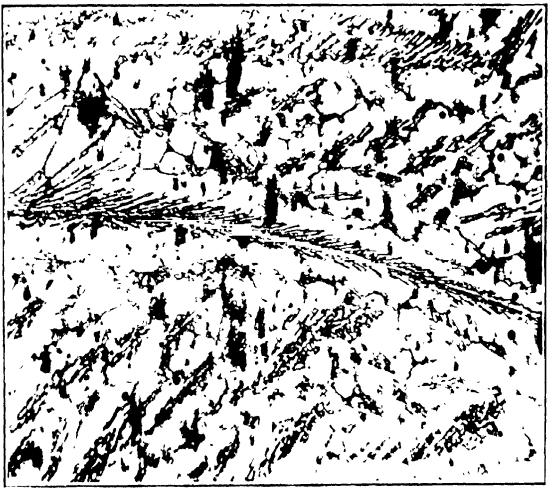
Influence of Heat Treatment on Steel containing 1·5 per cent. of Carbon.

No. 1.



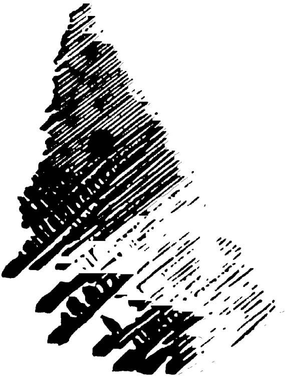
Crystallite Structure. × 1000.

No. 2.



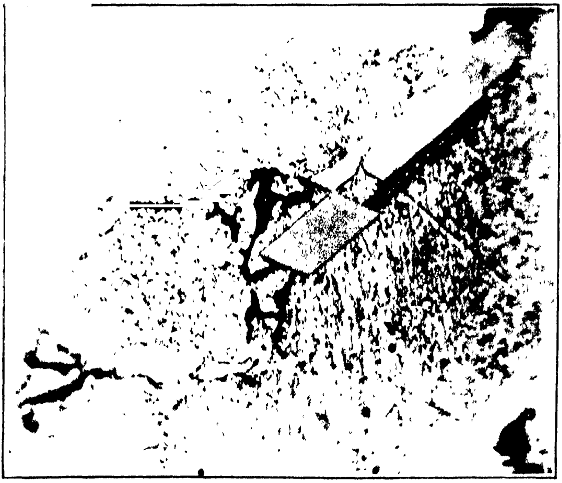
Crystallite Structure. × 100.

No 3.



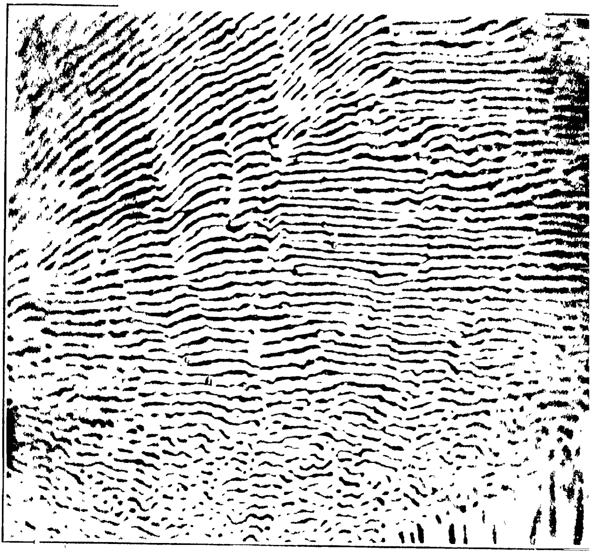
Metallic Crystallite separated from an Alloy by Solution in Acid. × 10.

No. 4.



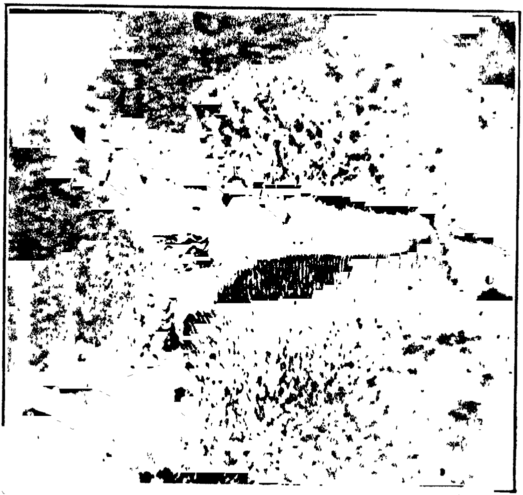
Aluminium-cobalt Alloy containing 10 per cent. Cobalt, showing Idiomorphic Crystal of the Compound Al_6Co. × 1000.

No. 5.

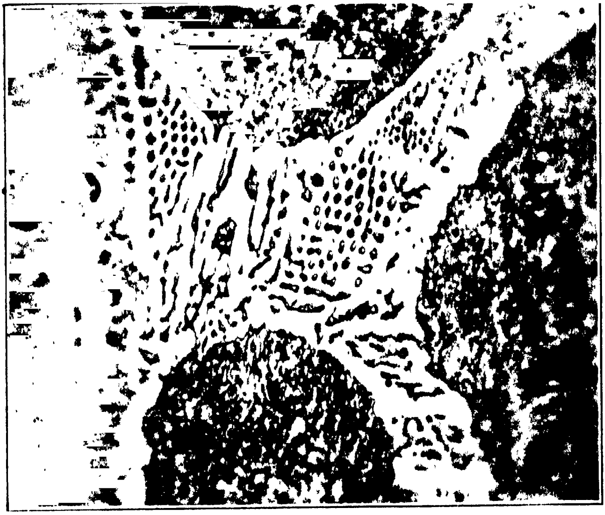


Laminated Eutectic Structure. × 1000.

No. 6.

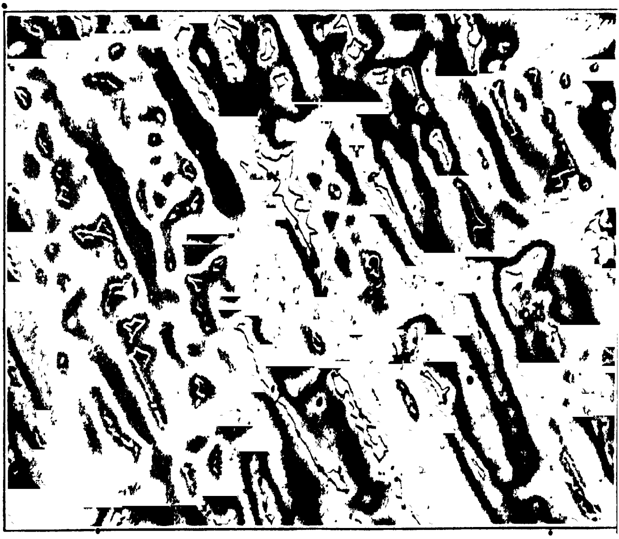


Fringe of Phospho-carbide Eutectic in Grey Iron. × 1000.



Phosphide Eutectic in Grey Iron. × 1000

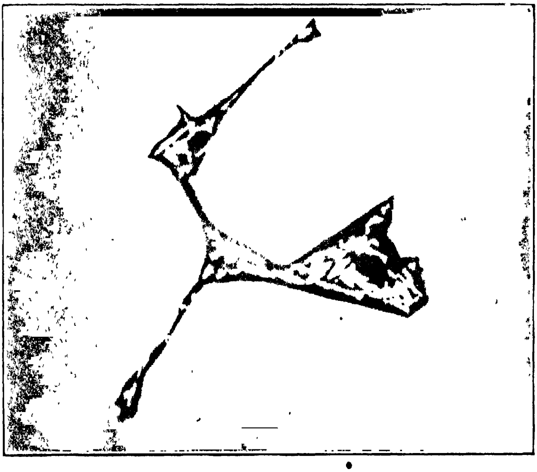
No. 8.



Gun-metal containing 12 per cent. of Tin, slowly cooled. × 100.

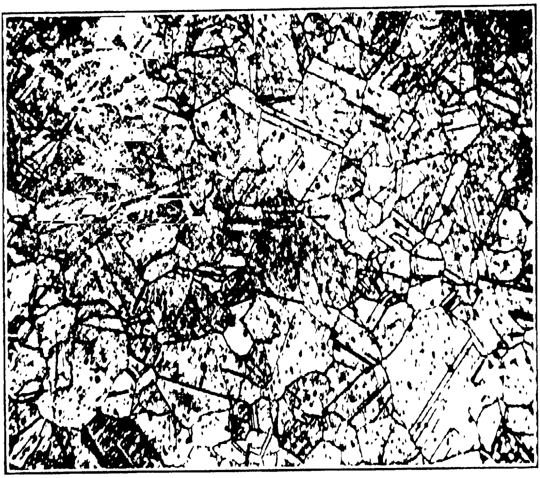
Gun-metal containing 12 per cent. of Tin, quickly cooled. × 100.

No. 10.



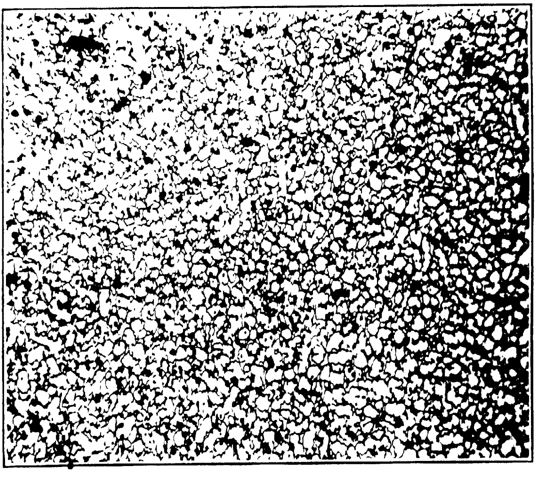
$SnCu_4$ Constituent in Gun-metal containing 12 per cent. of Tin.
Heat tinted. × 1000.

No. 11.



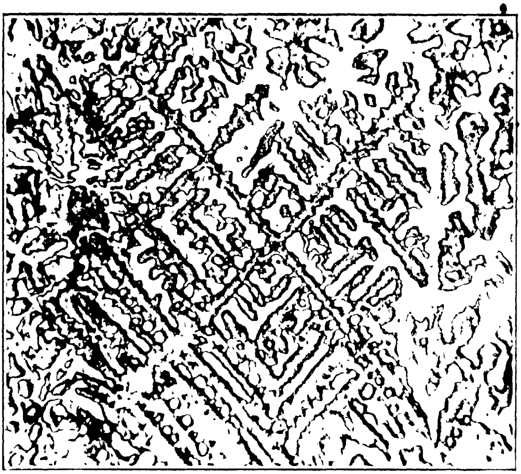
Rolled Brass containing 30 per cent. of Zinc. × 100

No 12.



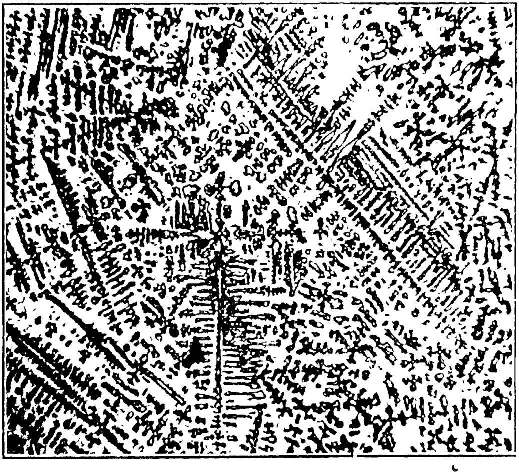
Muntz Metal, rolled. × 100.

No. 13.



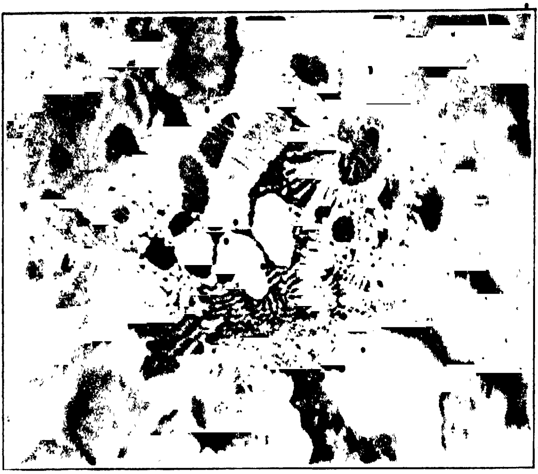
Cast Phosphor-bronze containing 10 per cent of Tin and 0·7 per cent. of Phosphorus. ×100.

No. 14.



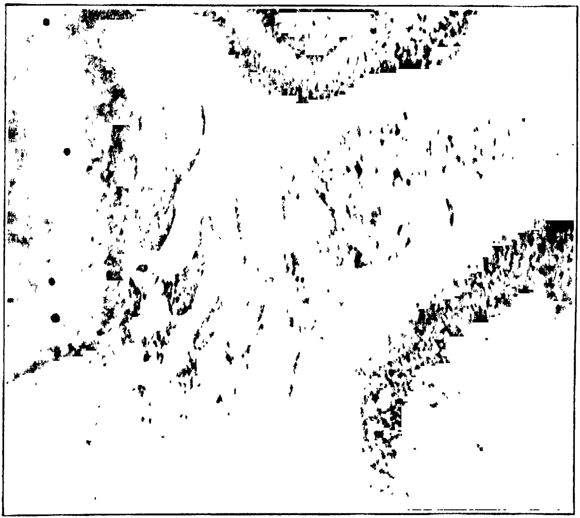
Cast Phosphor-bronze containing 10 per cent. of Tin and 1·5 per cent. of Phosphorus. ×100.

No. 15.

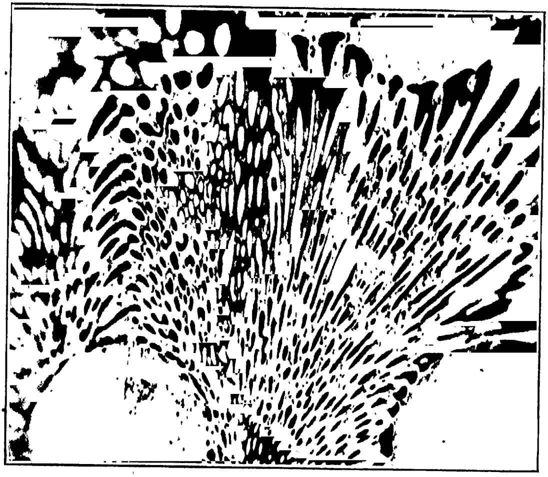


Cast Phosphor-bronze containing 1·5 per cent. of Phosphorus and 10 per cent. of Tin. × 1000

No. 16.

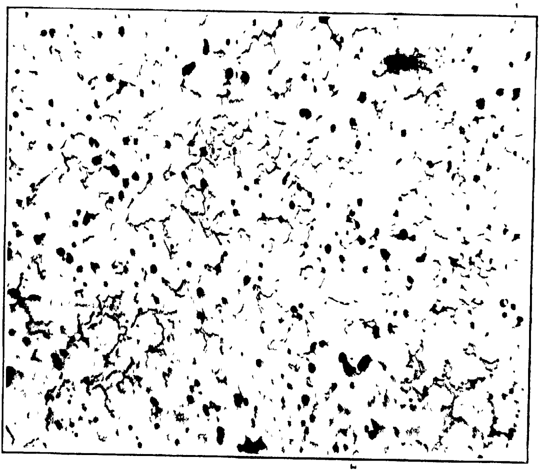


Cast Phosphor-bronze containing 1·5 per cent. Phosphorus. Heat-tinted. The dark constituent is the phosphide. × 1000.



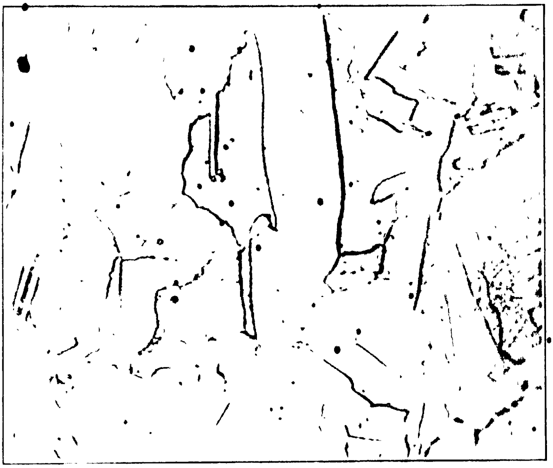
Eutectic of the two Compounds $SnCu_4$ and Cu_3P. × 1000.

No 18.



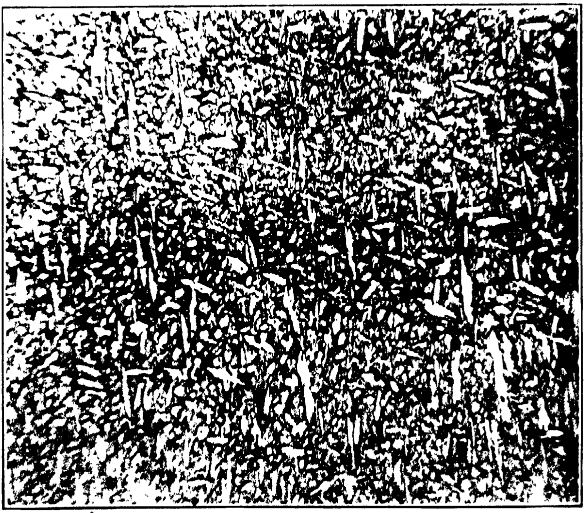
Phosphor-bronze containing Lead, unetched. × 100.

No. 19.



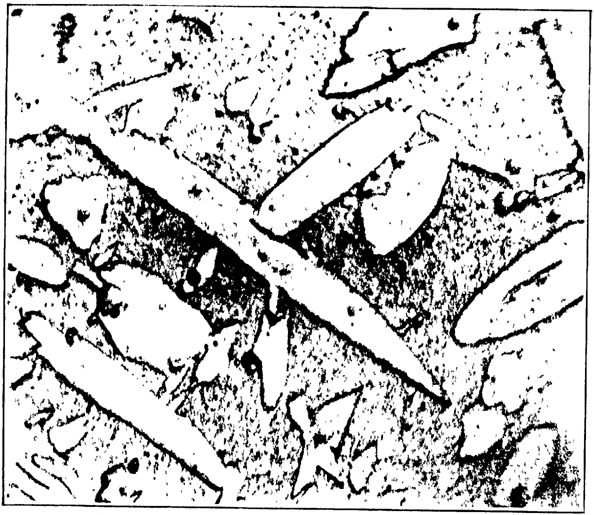
Manganese bronze Firebox Stay containing 4 per cent. of Manganese. × 1000.

No. 20.



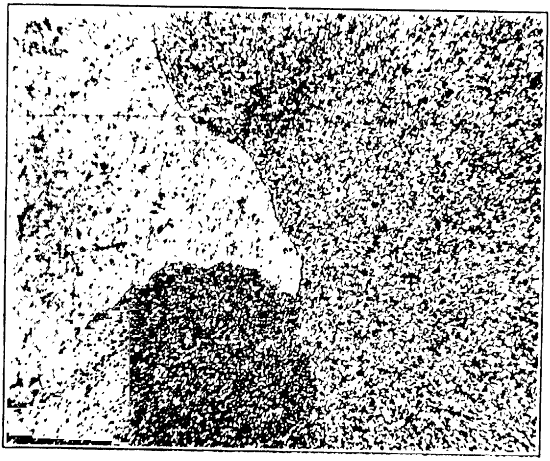
Manganese-bronze, rolled. × 100.

No. 21.



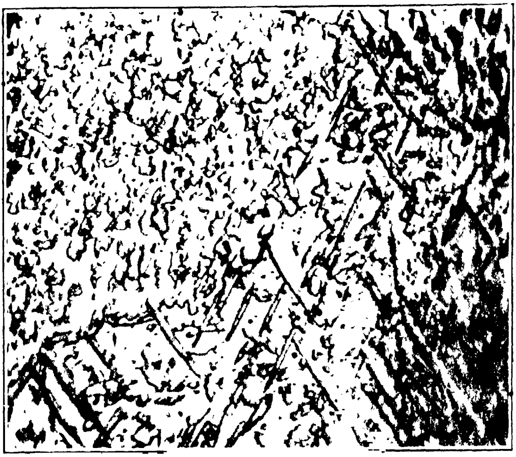
Manganese-bronze, rolled × 1000.

No. 22.



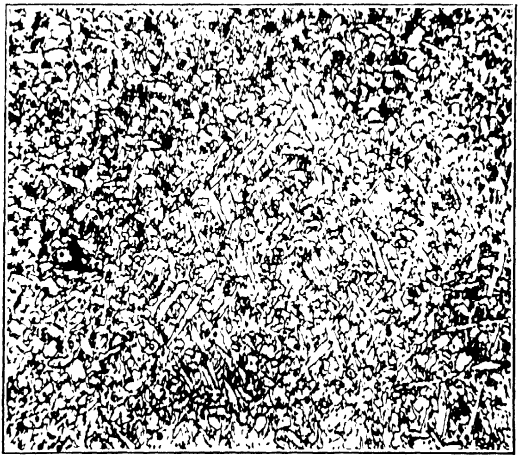
"Immadium I." Bronze. × 100.

No. 23.



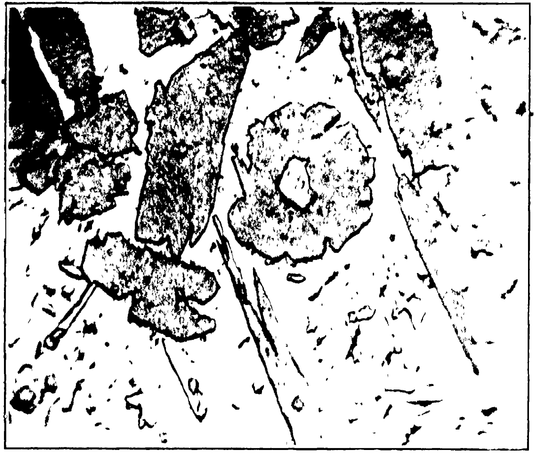
"Immadium I." Bronze. ×1000.

No. 24.



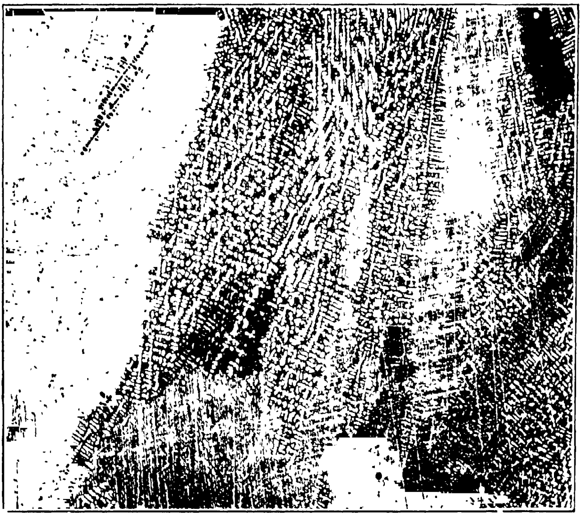
"Immadium II." Bronze. ×100.

No. 25.



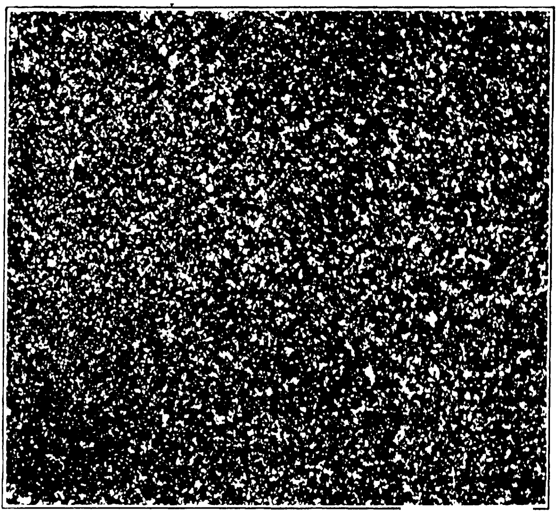
"Immadium II." Bronze. × 1000.

No. 26.

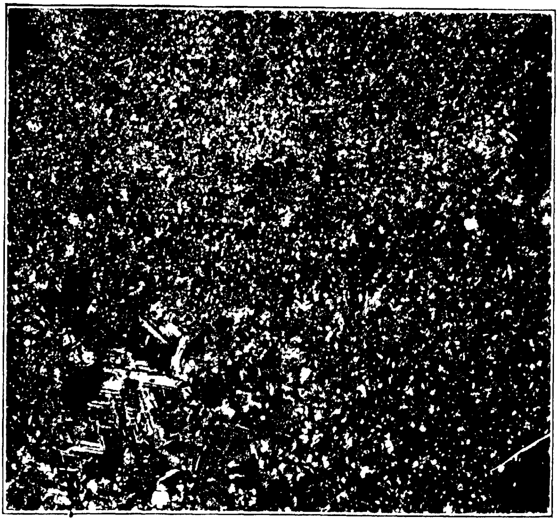


Aluminium-bronze containing 7·5 per cent. of Aluminium. Cast. × 10.

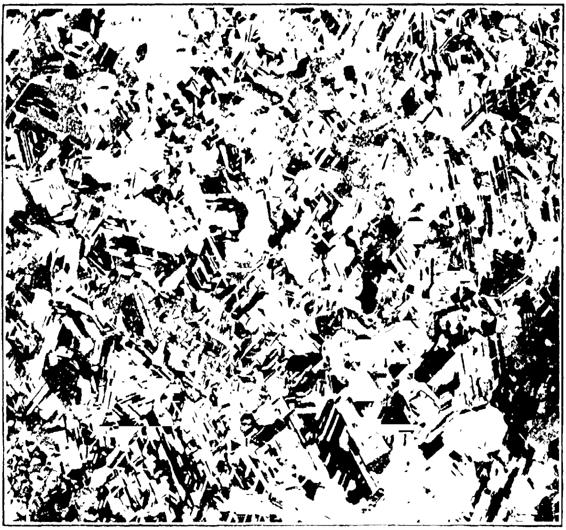
No. 27.



Rolled Aluminium bronze containing 7.5 per cent. of Aluminium. × 10.
No. 28.

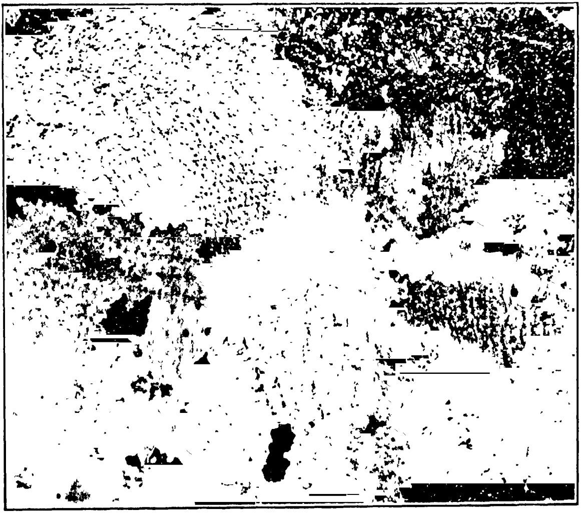


Aluminium-bronze containing 7.5 per cent. of Aluminium. Same as No. 28 after Annealing. × 10.

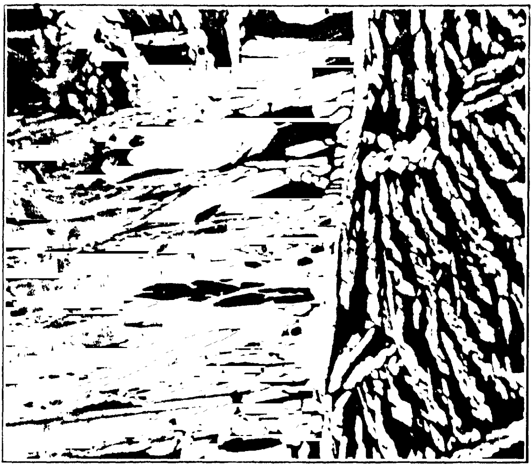


Aluminium-bronze containing 7·5 per cent. of Aluminium. Same as No. 29 after further Annealing. × 10.

No. 30.

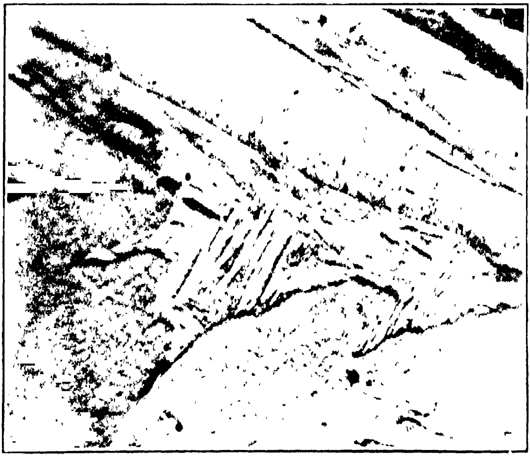


Aluminium-bronze containing 7·5 per cent. of Aluminium. Same as No. 30,

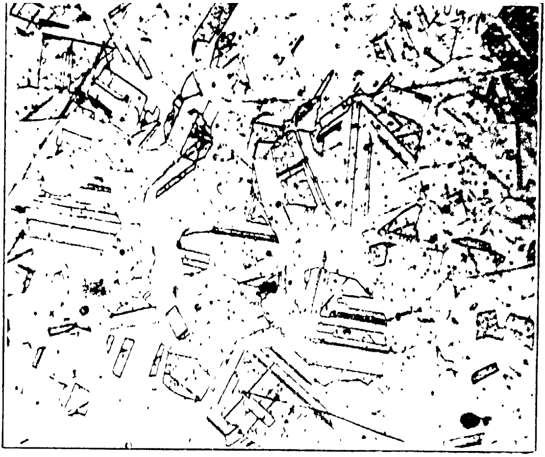


Aluminium-bronze containing 10 per cent of Aluminium × 100.

No. 32.

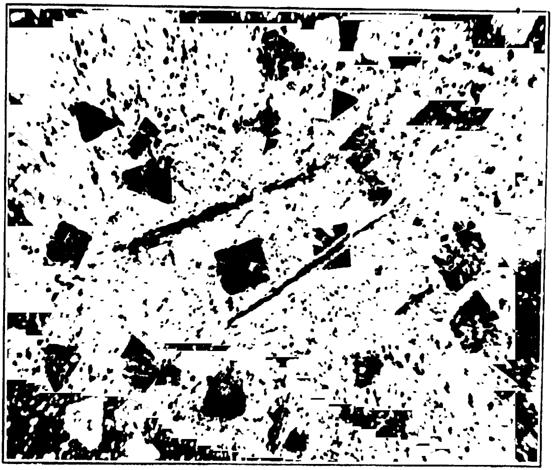


Aluminium-bronze containing 10 per cent. of Aluminium, showing the β Constituent. × 1000



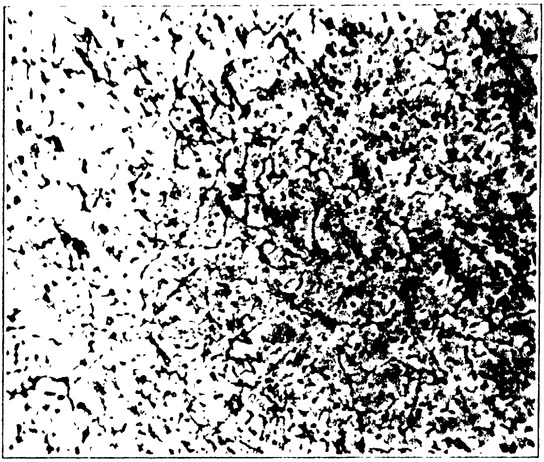
Rolled German Silver. × 100.

No. 34.



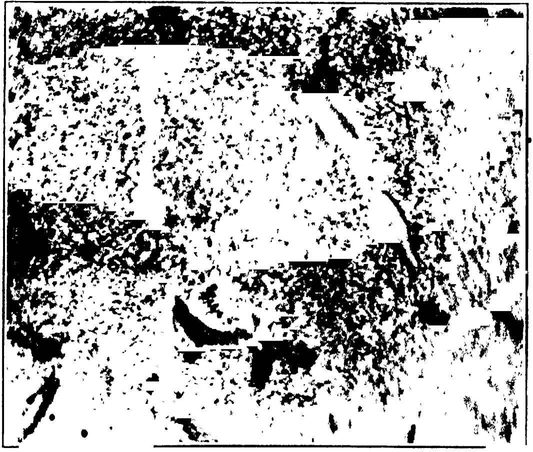
Tin-copper-antimony Bearing Metal. × 50.

No. 35.



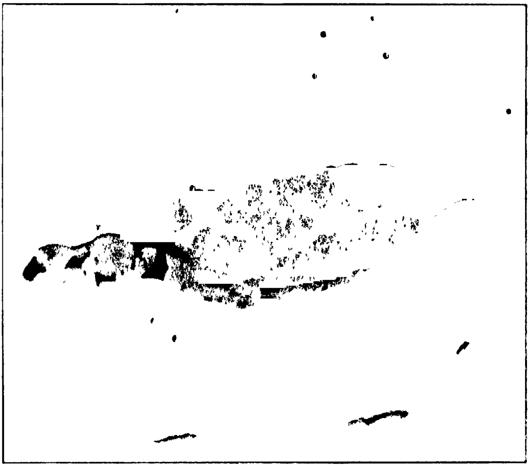
"Magnalium X," Cast. × 100.

No. 36.



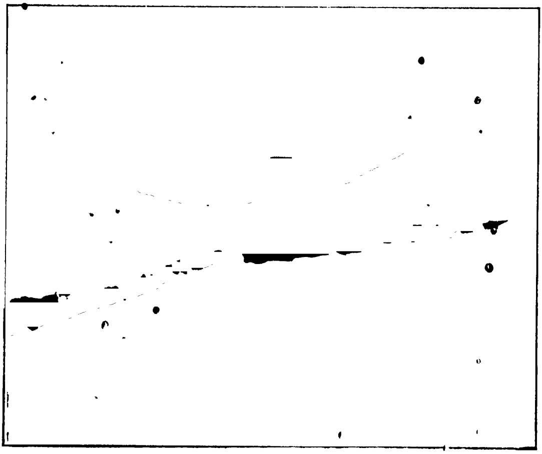
"Magnalium X," Cast. × 1000.

No. 37.



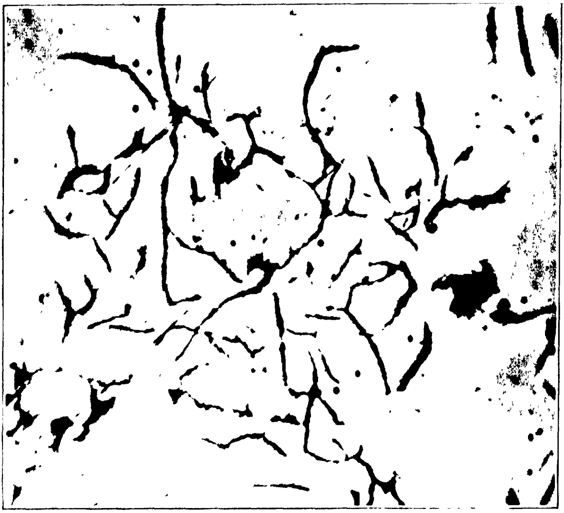
Manganese Sulphide and Silicate occurring together in Steel. × 1000.

No. 38.



Mild Steel, unetched, showing Sulphide of Manganese (the lighter constituent) and Silicate of Iron. × 1000.

No. 39



Graphite in Grey Iron. × 100

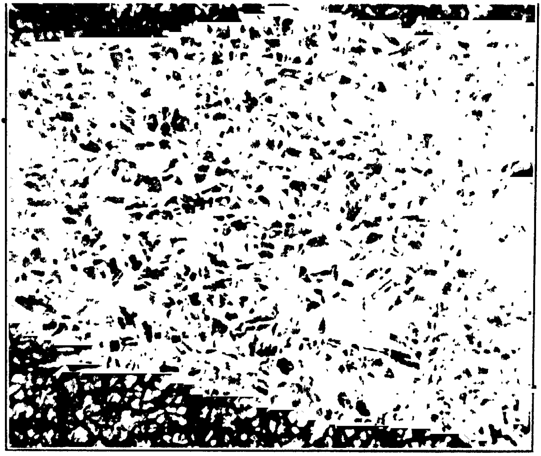
No. 40.

Steel containing Slag polished in Relief. × 100.

No. 41.

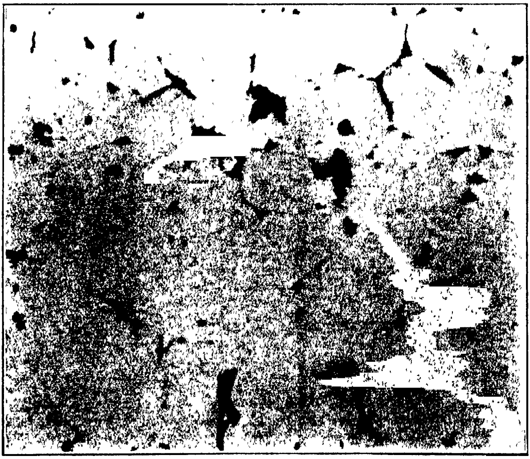
Steel containing 0·45 per cent. of Carbon quenched from 730°. The dark constituent is Troostite.

No. 42.



Rolled Muntz Metal Sheet ×100.

No. 43.

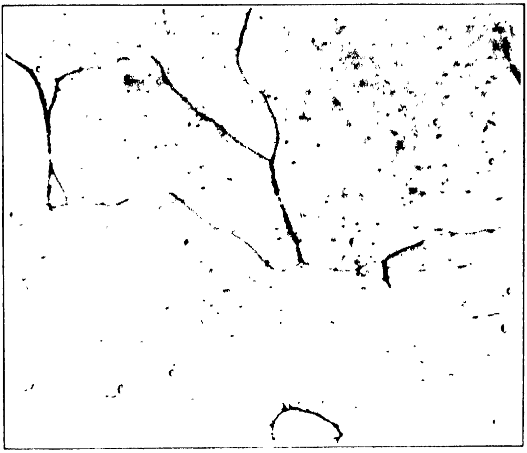


Oxidised Brass Casting. ×100.

No. 44.

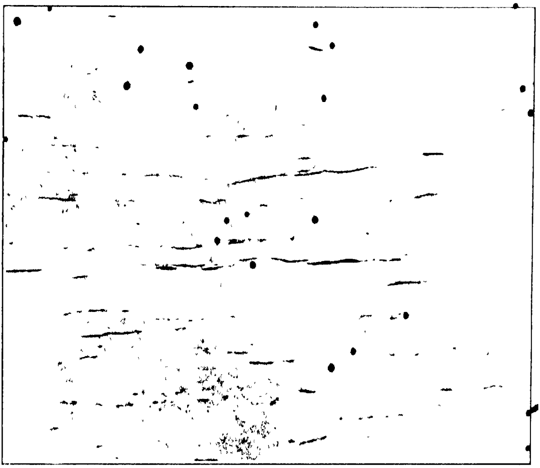
Oxidised Brass Casting. × 1000.

No. 45.



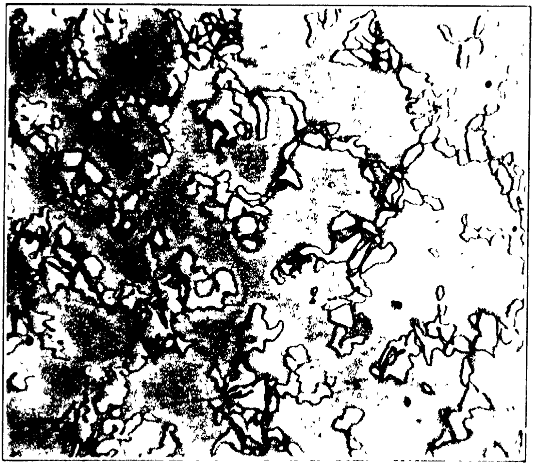
Overheated Steel showing complete Segregation of Carbide between the Crystal Boundaries. × 100

No. 46.



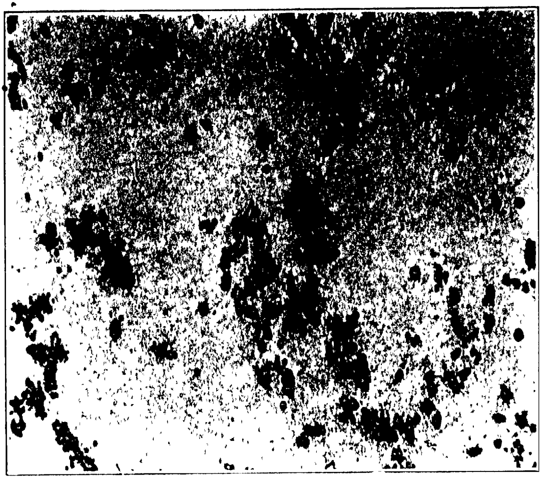
Manganese Sulphide Threads in Rolled Steel × 100

No. 47.



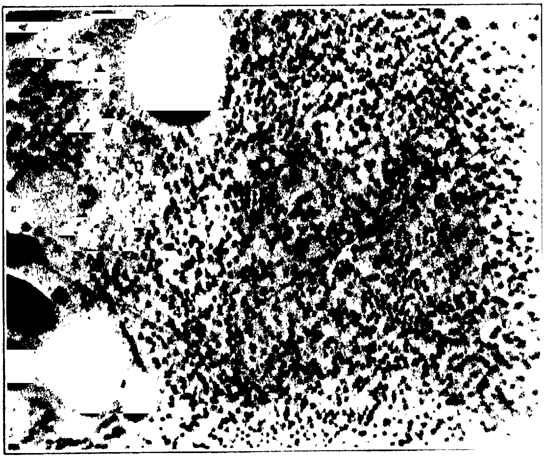
Massive Phosphide of Copper in Copper containing 5 per cent. of Tin × 100.

No. 48.



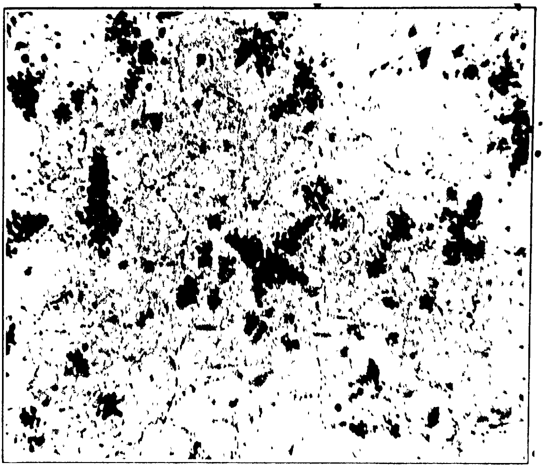
Dendrites of Copper Oxide in a Ground Mass of Eutectic. × 100.

No. 49.



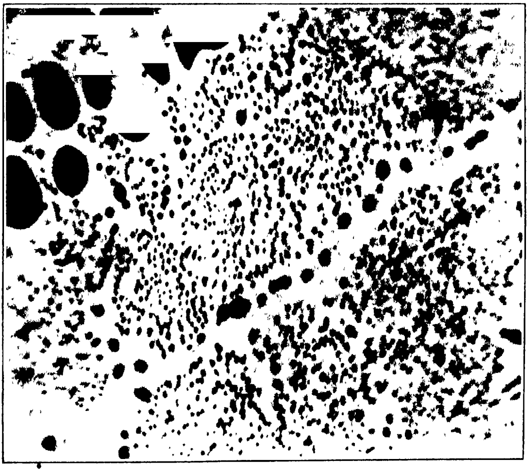
Eutectic of Copper and Copper Oxide in No. 49. × 1000.

No. 50.



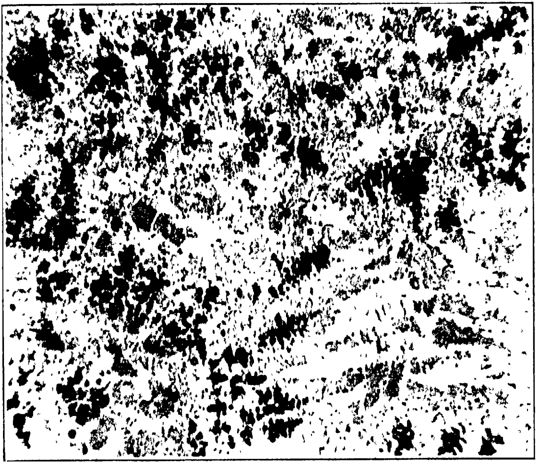
Same as No. 19 but with 0·08 per cent. Arsenic, showing Coalescence of Copper Oxide Particles in the Eutectic. × 100

No. 51.



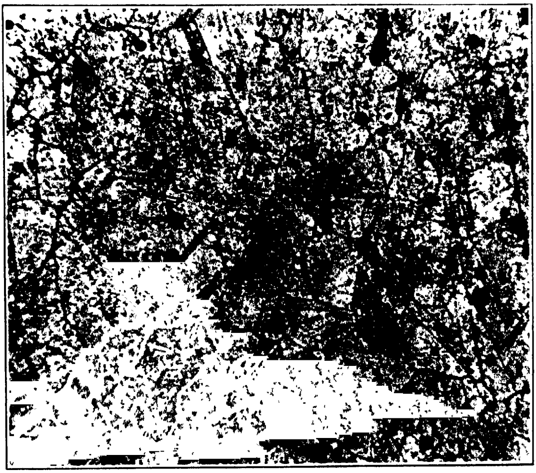
Same as No. 51, showing Coalescence of Copper Oxide Particles at Higher Magnification. × 1000.

No. 52.



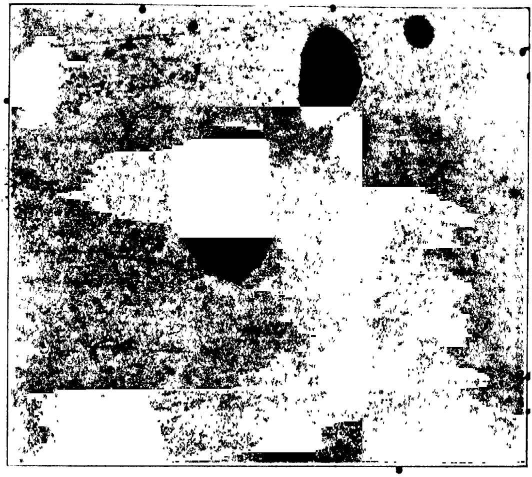
Same as No. 51 but with further addition of Arsenic, showing partial Disappearance of Eutectic due to Coalescence of Oxide Particles. × 100.

No. 53.



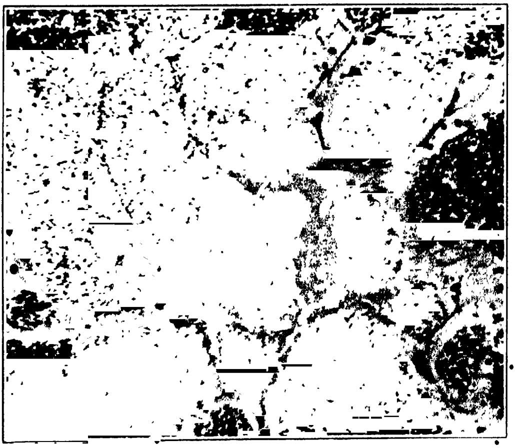
Copper Firebox Plate. × 100.

No. 54.



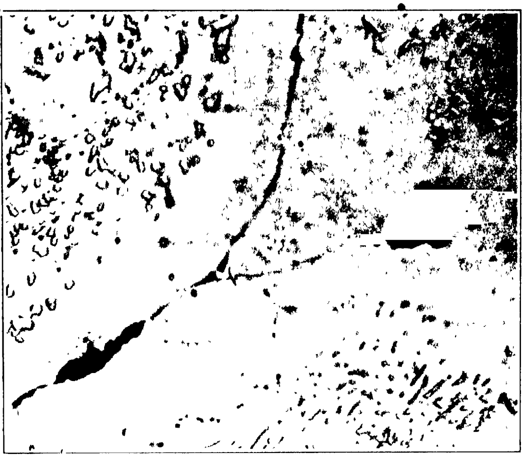
Copper Oxide in a Firebox Plate. × 1000.

No 55.



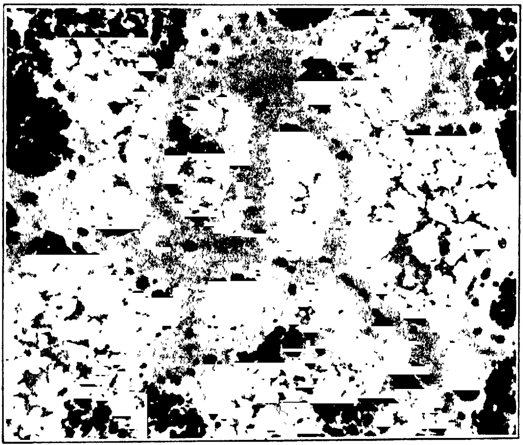
Cast Steel showing Network of Silico-sulphide Slag. × 100.

No. 56.

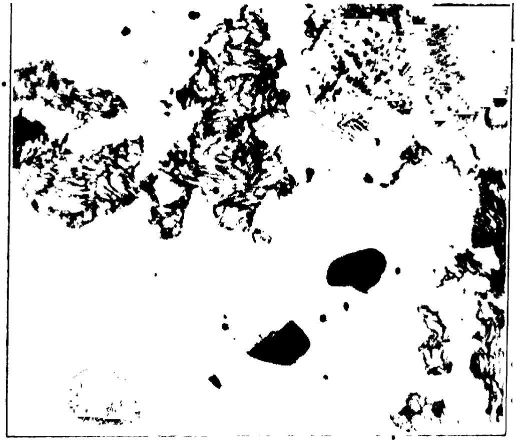


Same as No. 56 but more highly magnified, showing Network of Silico-sulphide Slag and Granular Carbide × 1000.

No. 57

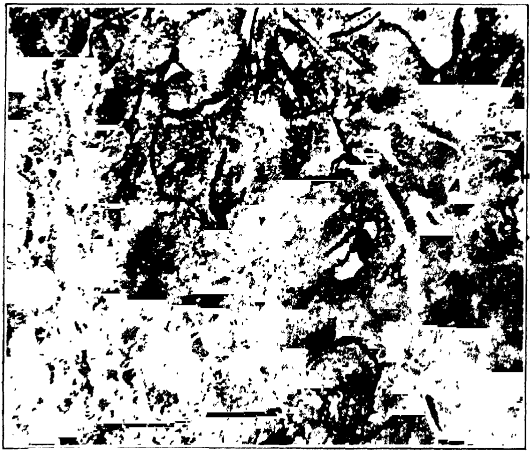


Cast Steel same as No. 56 but after annealing, showing isolated Masses of Manganese Sulphide replacing Network of Silico-sulphide. × 100.



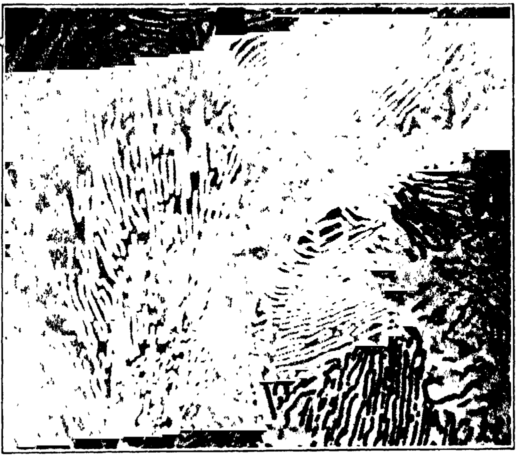
Same as No. 58 but more highly magnified, showing Manganese Sulphide and well-defined Pearlite × 1000.

No. 59



Grey Iron showing Graphite, Pearlite, and Lakes of Phosphide Eutectic. × 100.

No. 60.

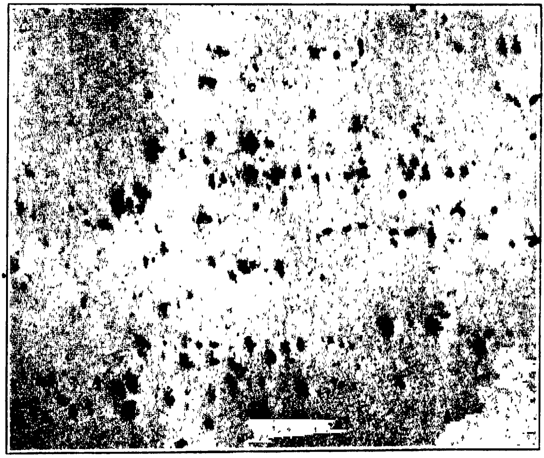


Same as No. 60 but more highly magnified, showing Phosphide Eutectic (globular) surrounded by Pearlite Eutectoid (laminated). × 1000.

No 61.

High Phosphorus Pig-iron, showing Pearlite surrounded by Phosphide Eutectic. × 1000.

No. 62.



Section of copper firebox containing 0·12 per cent. oxygen and 0·40 per cent arsenic, polished but unetched, showing copper oxide. × 100.

No 63.